```
=> fil reg
FILE 'REGISTRY' ENTERED AT 07:39:32 ON 13 DEC 2007
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Property values tagged with IC are from the ZIC/VINITI data file
provided by InfoChem.

STRUCTURE FILE UPDATES:   12 DEC 2007  HIGHEST RN 957825-32-0
DICTIONARY FILE UPDATES:  12 DEC 2007  HIGHEST RN 957825-32-0

New CAS Information Use Policies, enter HELP USAGETERMS for details.

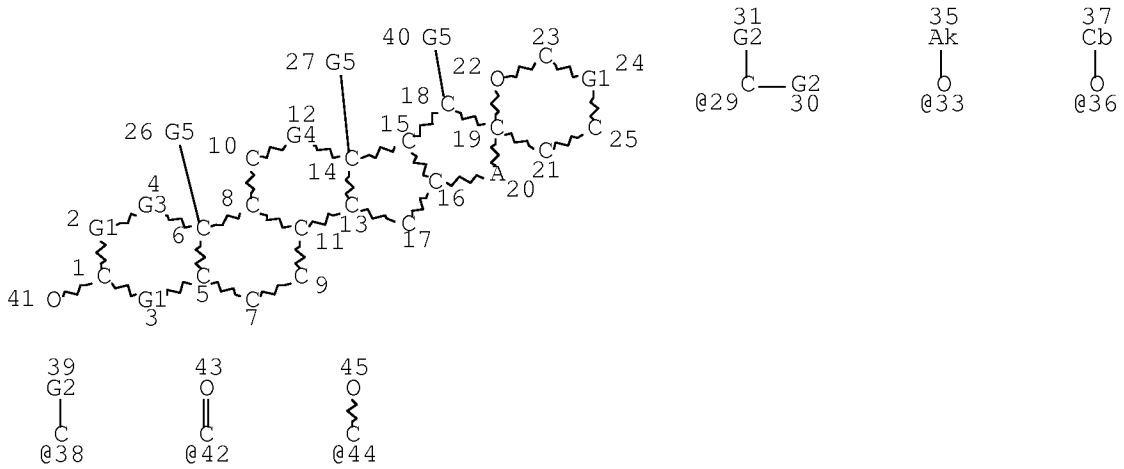
TSCA INFORMATION NOW CURRENT THROUGH June 29, 2007

  Please note that search-term pricing does apply when
  conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and
predicted properties as well as tags indicating availability of
experimental property data in the original document.  For information
on property searching in REGISTRY, refer to:

http://www.cas.org/support/stngen/stndoc/properties.html

=> d sta que l8
L1              STR
```

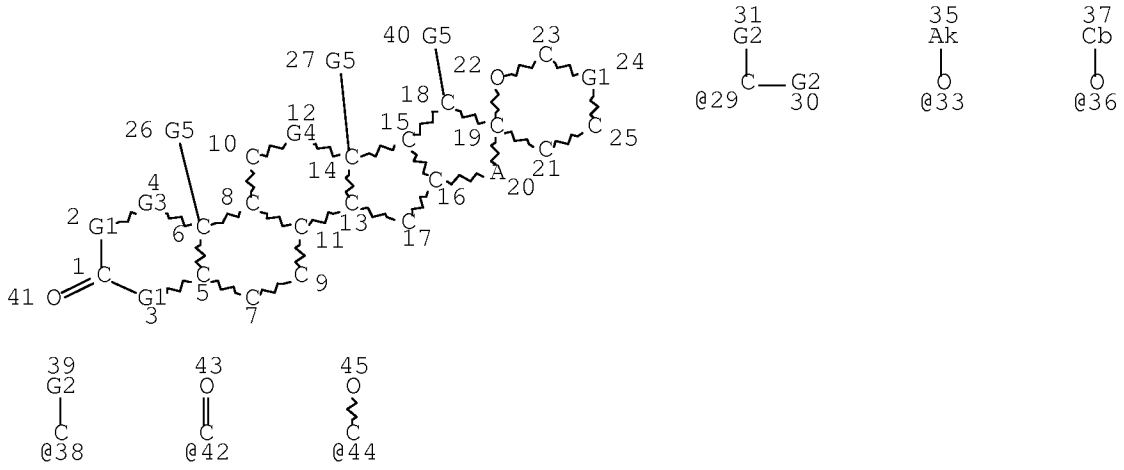



```
VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1  RC AT  41
CONNECT IS M1  RC AT  45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
```

RSPEC 1
NUMBER OF NODES IS 42

STEREO ATTRIBUTES: NONE
L2 2639 SEA FILE=REGISTRY CSS FUL L1
L3 STR

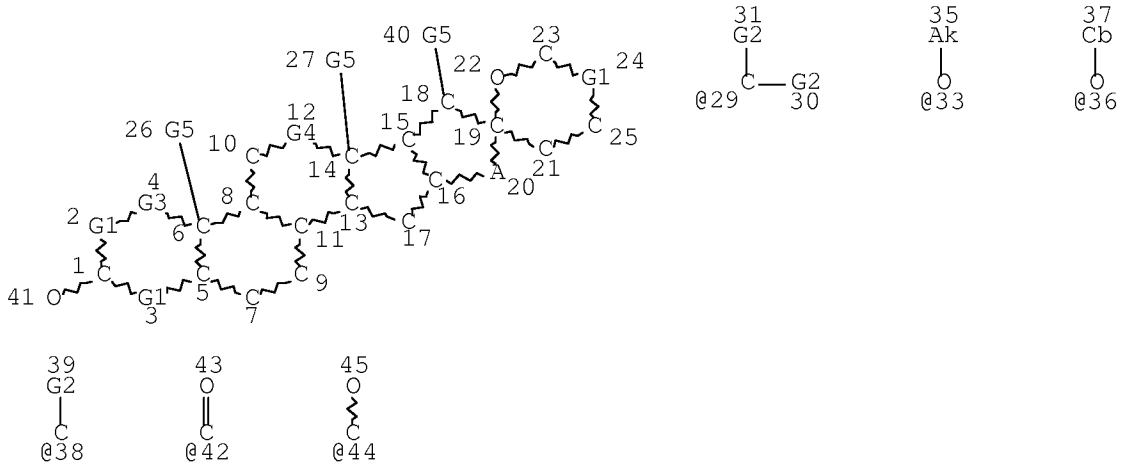


VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 41
CONNECT IS M1 RC AT 45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 42

STEREO ATTRIBUTES: NONE
L5 134 SEA FILE=REGISTRY SUB=L2 CSS FUL L3
L8 131 SEA FILE=REGISTRY ABB=ON PLU=ON L5 NOT (T/ELS OR 14C#)

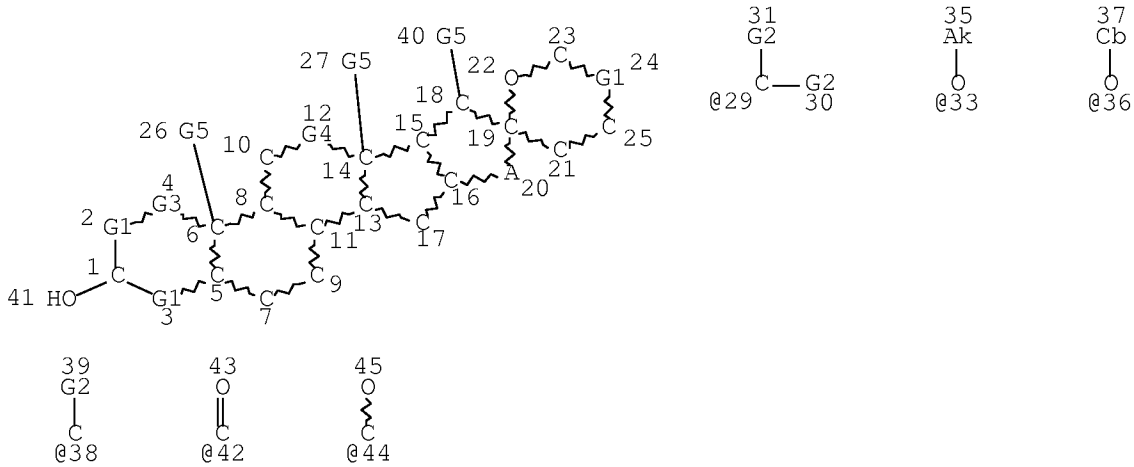
=> d sta que l18
L1 STR



VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 41
CONNECT IS M1 RC AT 45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 42

STEREO ATTRIBUTES: NONE
L2 2639 SEA FILE=REGISTRY CSS FUL L1
L9 STR



VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44

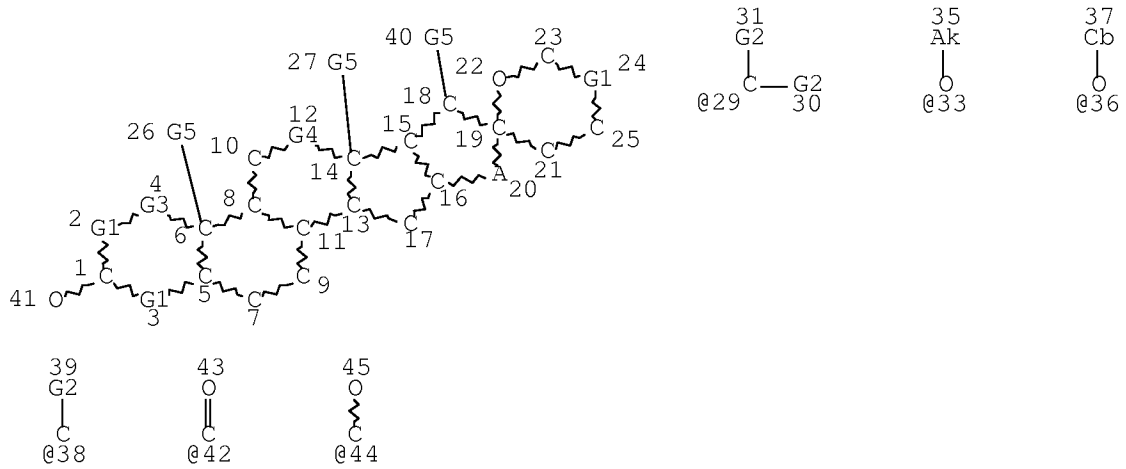
VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 42

STEREO ATTRIBUTES: NONE
L11 351 SEA FILE=REGISTRY SUB=L2 CSS FUL L9
L12 23 SEA FILE=REGISTRY ABB=ON PLU=ON L11 AND NC>=2
L13 328 SEA FILE=REGISTRY ABB=ON PLU=ON L11 NOT L12
L14 295 SEA FILE=REGISTRY ABB=ON PLU=ON L13 NOT ((D OR T)/ELS OR 11C# OR 13C# OR 14C# OR C11# OR C13# OR C14# OR LABELED)
L15 12 SEA FILE=REGISTRY ABB=ON PLU=ON L14 AND IDS/CI
L16 283 SEA FILE=REGISTRY ABB=ON PLU=ON L14 NOT L15
L17 3 SEA FILE=REGISTRY ABB=ON PLU=ON L16 AND NR>=7
L18 280 SEA FILE=REGISTRY ABB=ON PLU=ON L16 NOT L17

=> d sta que l38
L38 4 SEA FILE=REGISTRY ABB=ON PLU=ON 126-18-1 OR 470-03-1 OR 16653-88-6 OR 126-19-2

=> d sta que l26
L1 STR

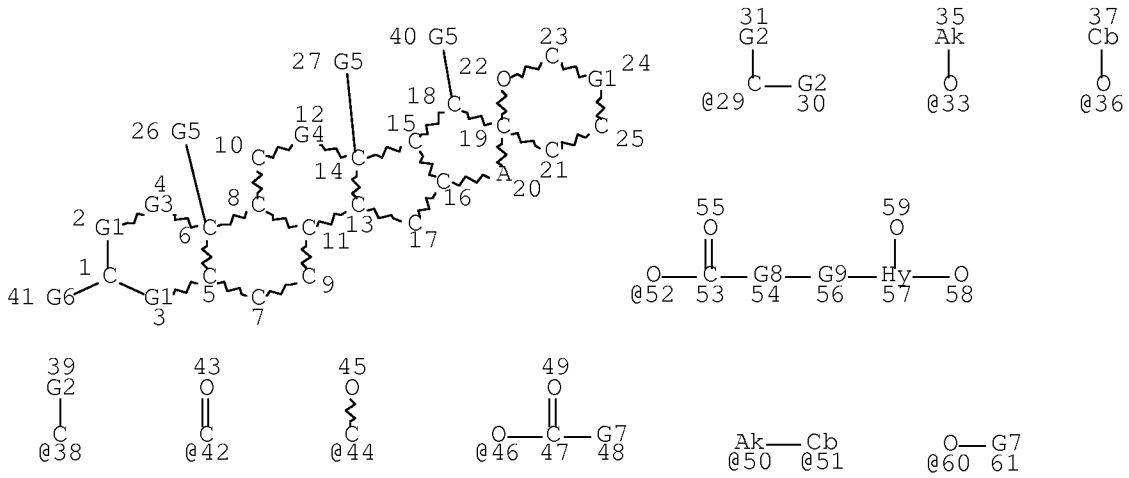


VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 41
CONNECT IS M1 RC AT 45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RSPEC 1
NUMBER OF NODES IS 42

STEREO ATTRIBUTES: NONE
L2 2639 SEA FILE=REGISTRY CSS FUL L1
L21 STR

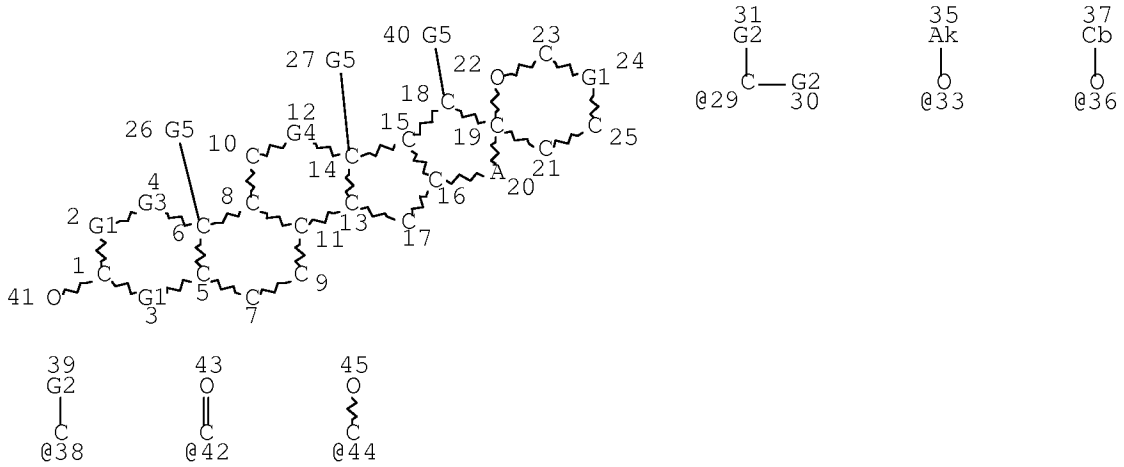


VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
VAR G6=46/52/60
VAR G7=AK/CB/50/51
REP G8=(0-1) O
REP G9=(0-1) C
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 45
CONNECT IS M1 RC AT 51
CONNECT IS M1 RC AT 57
CONNECT IS M1 RC AT 58
CONNECT IS M1 RC AT 59
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED
ECOUNT IS M1 O AT 57

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 58

STEREO ATTRIBUTES: NONE
L23 324 SEA FILE=REGISTRY SUB=L2 CSS FUL L21
L24 12 SEA FILE=REGISTRY ABB=ON PLU=ON L23 AND NC>=2
L25 64 SEA FILE=REGISTRY ABB=ON PLU=ON L23 AND NR>=7
L26 52 SEA FILE=REGISTRY ABB=ON PLU=ON L25 NOT L24

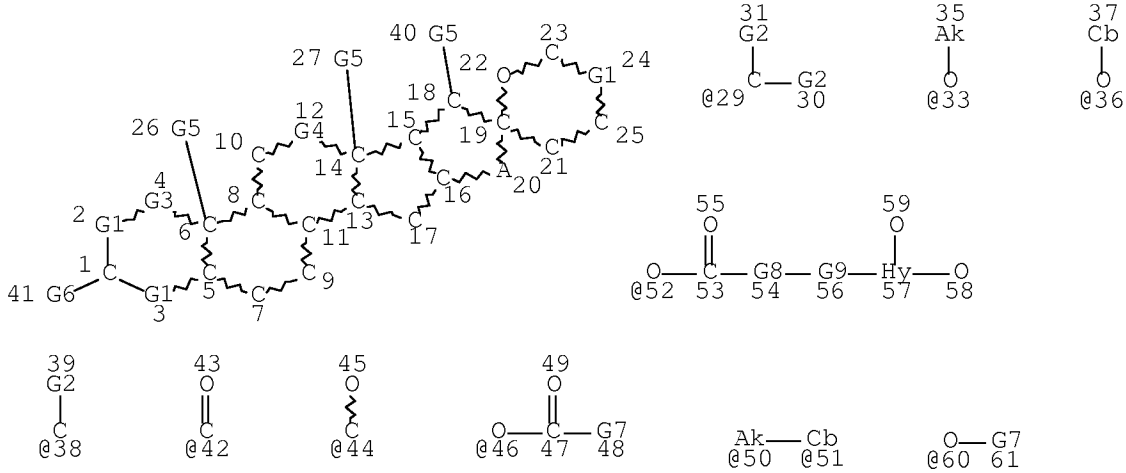
=> d sta que l28
L1 STR



VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 41
CONNECT IS M1 RC AT 45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 42

STEREO ATTRIBUTES: NONE
L2 2639 SEA FILE=REGISTRY CSS FUL L1
L21 STR



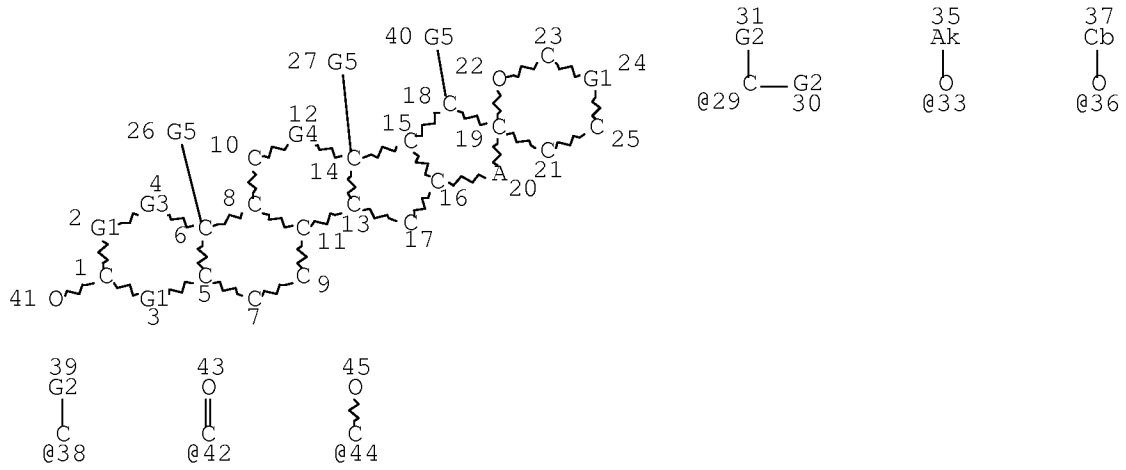
VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44

```
VAR G5=H/AK
VAR G6=46/52/60
VAR G7=AK/CB/50/51
REP G8=(0-1) O
REP G9=(0-1) C
NODE ATTRIBUTES:
CONNECT IS M1  RC AT  45
CONNECT IS M1  RC AT  51
CONNECT IS M1  RC AT  57
CONNECT IS M1  RC AT  58
CONNECT IS M1  RC AT  59
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED
ECOUNT  IS M1 O  AT  57

GRAPH ATTRIBUTES:
RSPEC   1
NUMBER OF NODES IS  58

STEREO ATTRIBUTES: NONE
L23         324 SEA FILE=REGISTRY SUB=L2 CSS FUL L21
L24          12 SEA FILE=REGISTRY ABB=ON  PLU=ON  L23 AND NC>=2
L25          64 SEA FILE=REGISTRY ABB=ON  PLU=ON  L23 AND NR>=7
L26          52 SEA FILE=REGISTRY ABB=ON  PLU=ON  L25 NOT L24
L27         299 SEA FILE=REGISTRY ABB=ON  PLU=ON  L23 NOT ((D OR T)/ELS OR
                11C# OR 13C# OR 14C# OR C11# OR C13# OR C14# OR LABELED)
L28         235 SEA FILE=REGISTRY ABB=ON  PLU=ON  L27 NOT (L24 OR L25 OR L26)

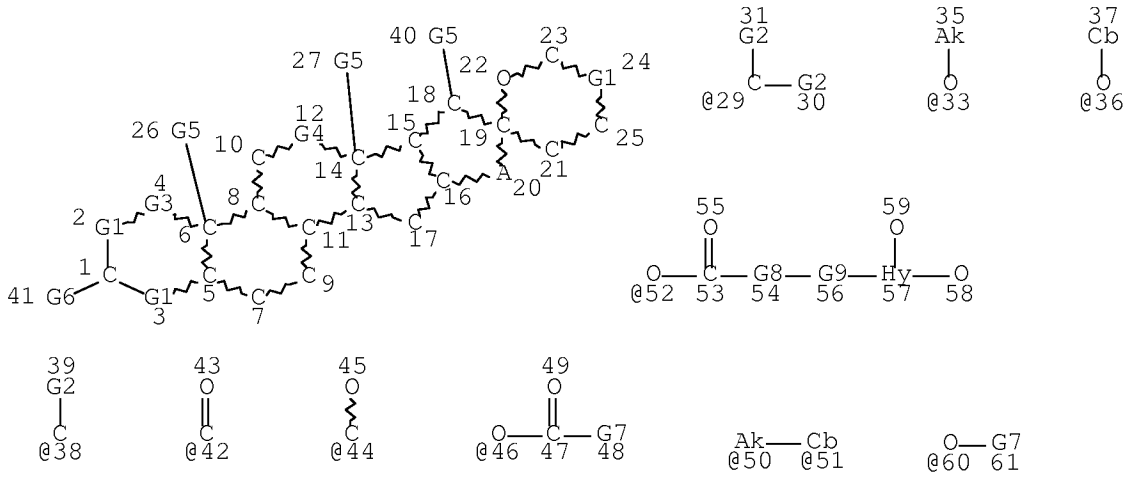

=> d sta que l37
L1              STR
```




```
VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1  RC AT  41
CONNECT IS M1  RC AT  45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED
```

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 42

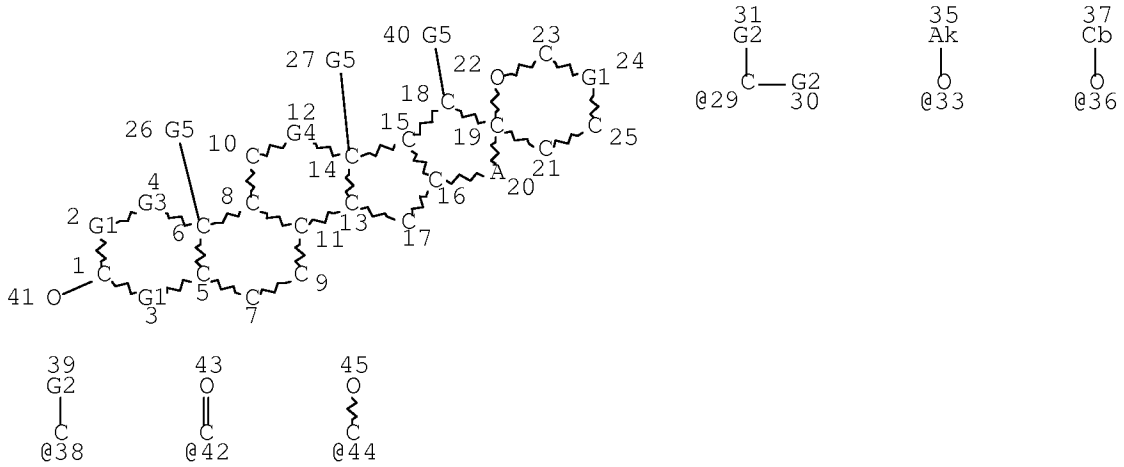
STEREO ATTRIBUTES: NONE
L2 2639 SEA FILE=REGISTRY CSS FUL L1
L21 STR



VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
VAR G6=46/52/60
VAR G7=AK/CB/50/51
REP G8=(0-1) O
REP G9=(0-1) C
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 45
CONNECT IS M1 RC AT 51
CONNECT IS M1 RC AT 57
CONNECT IS M1 RC AT 58
CONNECT IS M1 RC AT 59
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED
ECOUNT IS M1 O AT 57

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 58

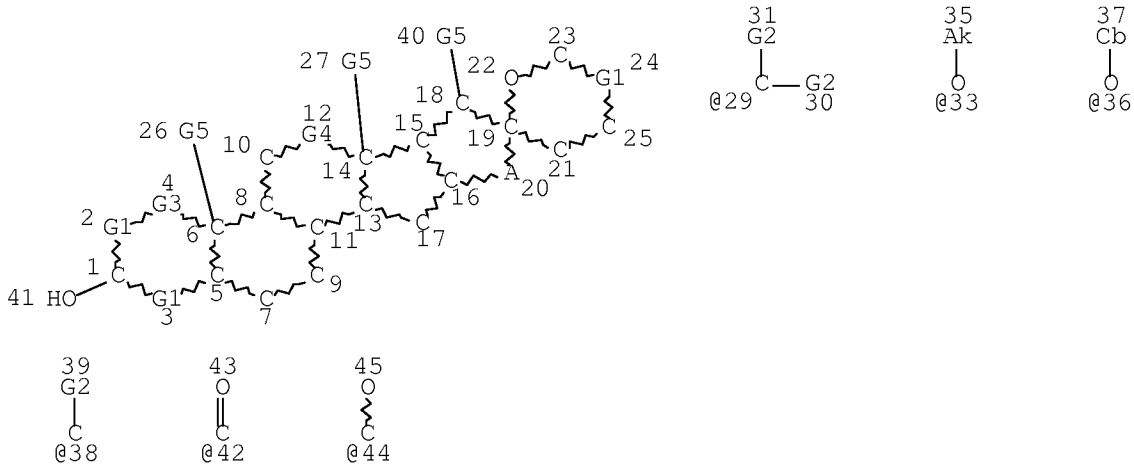
STEREO ATTRIBUTES: NONE
L23 324 SEA FILE=REGISTRY SUB=L2 CSS FUL L21
L29 STR



VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 41
CONNECT IS M1 RC AT 45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 42

STEREO ATTRIBUTES: NONE
L30 2505 SEA FILE=REGISTRY SUB=L2 CSS FUL L29
L31 STR

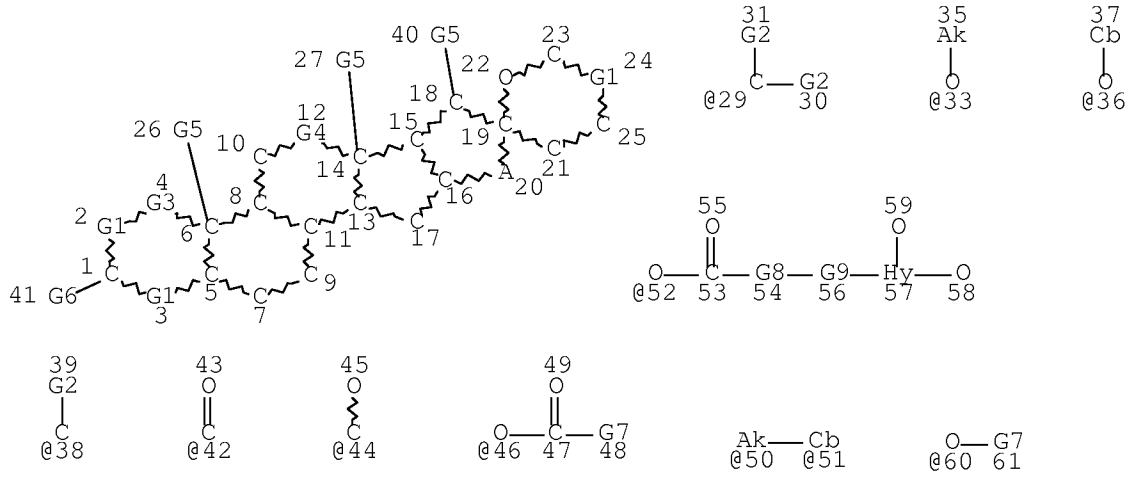


VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44

VAR G5=H/AK
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 45
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 42

STEREO ATTRIBUTES: NONE
L32 352 SEA FILE=REGISTRY SUB=L30 CSS FUL L31
L34 STR



VAR G1=C/38/29
VAR G2=AK/OH/33/36
VAR G3=C/38
VAR G4=C/38/29/42/44
VAR G5=H/AK
VAR G6=46/52/60
VAR G7=AK/CB/50/51
REP G8=(0-1) O
REP G9=(0-1) C
NODE ATTRIBUTES:
CONNECT IS M1 RC AT 45
CONNECT IS M1 RC AT 51
CONNECT IS M1 RC AT 57
CONNECT IS M1 RC AT 58
CONNECT IS M1 RC AT 59
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED
ECOUNT IS M1 O AT 57

GRAPH ATTRIBUTES:
RSPEC 1
NUMBER OF NODES IS 58

STEREO ATTRIBUTES: NONE
L35 339 SEA FILE=REGISTRY SUB=L2 CSS FUL L34
L36 15 SEA FILE=REGISTRY ABB=ON PLU=ON L35 NOT (L32 OR L23)
L37 14 SEA FILE=REGISTRY ABB=ON PLU=ON L36 NOT 14C

```
=> fil hcaplus
FILE 'HCAPLUS' ENTERED AT 07:40:03 ON 13 DEC 2007
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FILE LAST UPDATED: 12 Dec 2007  (20071212/ED)

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 This file contains CAS Registry Numbers for easy and accurate
 substance identification.

=> => d l71 bib abs hitind hitstr retable tot

L71  ANSWER 1 OF 4  HCAPLUS  COPYRIGHT 2007 ACS on STN
AN   2004:370948  HCAPLUS  Full-text
DN   140:375358
TI   Stereospecific reduction of sapogen-3-ones
IN   Gunning, Philip James; Tiffin, Peter David
PA   Phytotech Limited, UK
SO   PCT Int. Appl., 41 pp.
     CODEN: PIXXD2
DT   Patent
LA   English
FAN.CNT 1
     PATENT NO.          KIND   DATE        APPLICATION NO.        DATE
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             CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
             GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
             LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM,
             PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT,
             TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
         RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY,
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             FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR,
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     CN 1723218           A     20060118    CN 2003-824744         20030428 <--
     JP 2006507360        T     20060302    JP 2005-501542         20030428 <--
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	MX 2005PA04494	A	20050726	MX 2005-PA4494	20050427 <--
	US 2006041119	A1	20060223	US 2005-531086	20050621 <--
	IN 2007MN01247	A	20071019	IN 2007-MN1247	20070817 <--
PRAI	GB 2002-25106	A	20021028 <--		
	GB 2003-1505	A	20030122		
	WO 2003-GB1780	W	20030428		
	IN 2005-MN308	A3	20050420		

OS CASREACT 140:375358; MARPAT 140:375358

AB A method to stereospecifically prepare a steroidal sapogenin or a derivative thereof by reducing a 3-keto,5β-H steroidal sapogenin with a hindered organoborane or an organo-aluminum hydride. A 3β-hydroxy,5β-H steroidal sapogenin or derivative may be prepared by reducing the 3-keto,5β-H steroidal sapogenin using as reducing agent which is a relatively highly hindered organoborane reagent or by SN 2 inversion of a 3α-hydroxy,5β-H steroidal sapogenin or derivative The organo-aluminum hydride may be used to prepare a 3α,hydroxy,5β-H steroidal sapogenin or derivative The invention provides a convenient route to useful steroidal sapogenins such as sarsasapogenin, episarsasapogenin, smilagenin, epismilagenin and esters thereof, from readily available or easily prepared starting materials (e.g. diosgenone, prepared from diosgenin).

IC ICM C07J0071-00

CC 32-8 (Steroids)

ST stereospecific redn sapogenone; steroidal sapogenin prepn; smilagenin prepn; sarsasapogenin prepn

IT Steroids, preparation
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(sapogenins; stereospecific reduction of sapogen-3-ones)

IT Reduction
(stereoselective; stereospecific reduction of sapogen-3-ones)

IT Asymmetric synthesis and induction
(stereospecific reduction of sapogen-3-ones)

IT Sapogenins
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(steroidal; stereospecific reduction of sapogen-3-ones)

IT 470-03-1P, Episarsasapogenin
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(stereospecific reduction of sapogen-3-ones)

IT 96-47-9, 2-Methyltetrahydrofuran 108-88-3, Toluene, uses 109-87-5, Dimethoxymethane 109-99-9, Thf, uses 123-91-1, 1,4-Dioxane, uses 1634-04-4, tert-Butyl methyl ether
RL: NUU (Other use, unclassified); USES (Uses)
(stereospecific reduction of sapogen-3-ones)

IT 639-96-3, Sarsasapogenone 6870-79-7, Diosgenone
RL: RCT (Reactant); RACT (Reactant or reagent)
(stereospecific reduction of sapogen-3-ones)

IT 126-19-2P, Sarsasapogenin 512-07-2P, Smilagenone 16653-88-6P, Epismilagenin
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(stereospecific reduction of sapogen-3-ones)

IT 17476-04-9, Lithium tri-tert-butoxyaluminohydride 38721-52-7, Lithium tri-sec-butylborohydride 54575-49-4, Potassium tri-sec-butylborohydride 60217-34-7, Lithium triamylborohydride 63717-74-8, Borate(1-), hydrotriphenyl-,

lithium, (T-4)- 67276-04-4, Sodium tri-sec-butylborohydride 67966-25-0, Potassium trisamylborohydride 99747-36-1, Potassium triphenylborohydride
RL: RGT (Reagent); RACT (Reactant or reagent)
(stereospecific reduction of sapogen-3-ones)

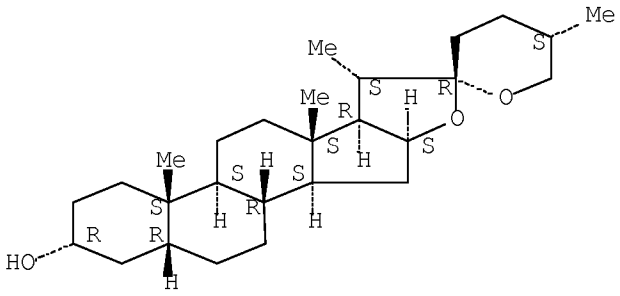
IT 126-18-1P, Smilagenin 4952-69-6P, Smilagenin benzoate
RL: SPN (Synthetic preparation); PREP (Preparation)
(stereospecific reduction of sapogen-3-ones)

IT 470-03-1P, Episarsasapogenin
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(stereospecific reduction of sapogen-3-ones)

RN 470-03-1 HCAPLUS

CN Spirostan-3-ol, (3α,5β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

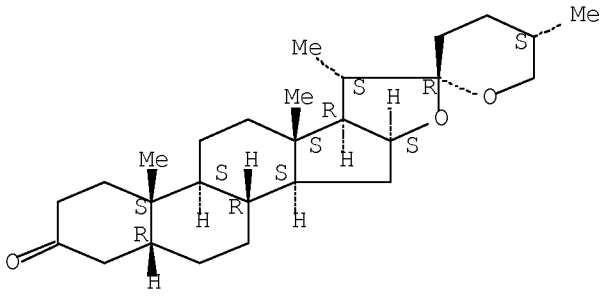


IT 639-96-3, Sarsasapogenone 6870-79-7, Diosgenone
RL: RCT (Reactant); RACT (Reactant or reagent)
(stereospecific reduction of sapogen-3-ones)

RN 639-96-3 HCAPLUS

CN Spirostan-3-one, (5β,25S)- (9CI) (CA INDEX NAME)

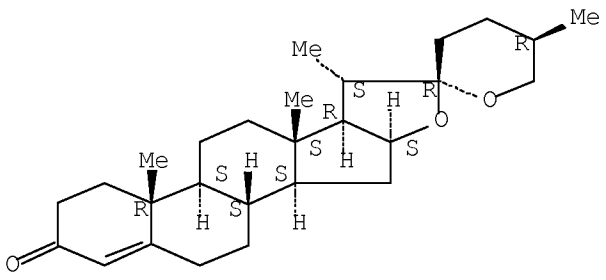
Absolute stereochemistry.



RN 6870-79-7 HCAPLUS

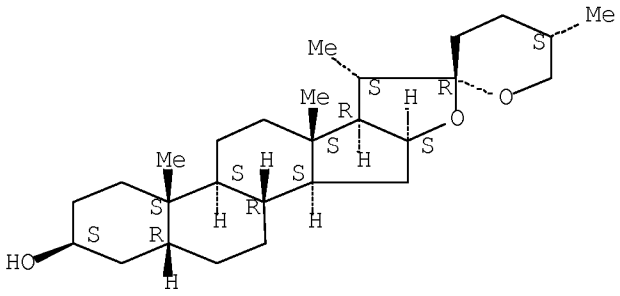
CN Spirost-4-en-3-one, (25R)- (CA INDEX NAME)

Absolute stereochemistry.



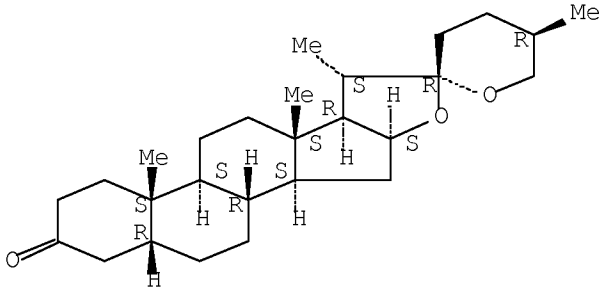
IT 126-19-2P, Sarsasapogenin 512-07-2P,
Smilagenone 16653-88-6P, Epismilagenin
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(stereospecific reduction of sapogen-3-ones)
RN 126-19-2 HCAPLUS
CN Spirostan-3-ol, (3β,5β,25S)- (CA INDEX NAME)

Absolute stereochemistry.



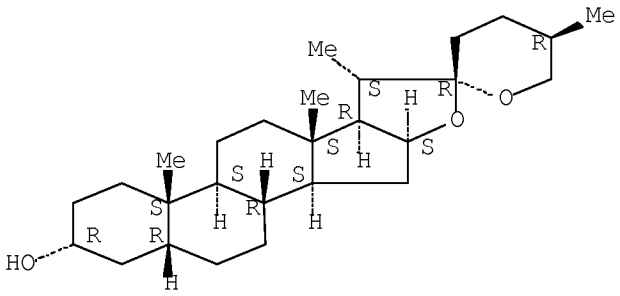
RN 512-07-2 HCAPLUS
CN Spirostan-3-one, (5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 16653-88-6 HCAPLUS
CN Spirostan-3-ol, (3α,5β,25R)- (9CI) (CA INDEX NAME)

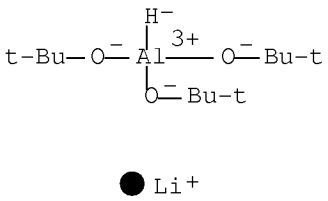
Absolute stereochemistry.



IT 17476-04-9, Lithium tri-tert-butoxyaluminohydride
38721-52-7, Lithium tri-sec-butylborohydride 54575-49-4,
Potassium tri-sec-butylborohydride 60217-34-7, Lithium
triamylborohydride 63717-74-8, Borate(1-), hydrotriphenyl-,
lithium, (T-4)- 67276-04-4, Sodium tri-sec-butylborohydride
67966-25-0, Potassium trisamylborohydride 99747-36-1,
Potassium triphenylborohydride
RL: RGT (Reagent); RACT (Reactant or reagent)
(stereospecific reduction of sapogen-3-ones)

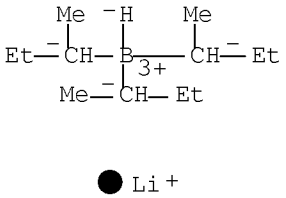
RN 17476-04-9 HCAPLUS

CN Aluminate(1-), hydrotris(2-methyl-2-propanolato)-, lithium (1:1), (T-4)-
(CA INDEX NAME)



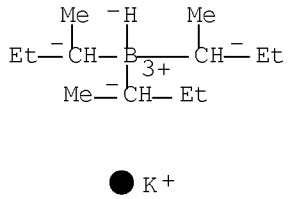
RN 38721-52-7 HCAPLUS

CN Borate(1-), hydrotris(1-methylpropyl)-, lithium (1:1), (T-4)- (CA INDEX
NAME)

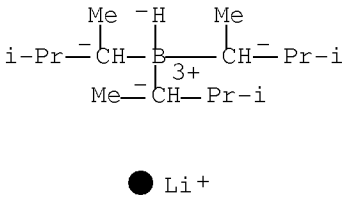


RN 54575-49-4 HCAPLUS

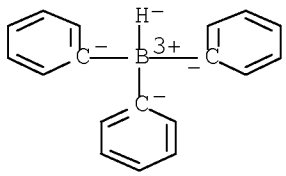
CN Borate(1-), hydrotris(1-methylpropyl)-, potassium (1:1), (T-4)- (CA INDEX
NAME)



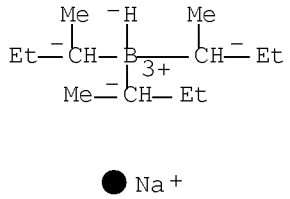
RN 60217-34-7 HCAPLUS
CN Borate(1-), tris(1,2-dimethylpropyl)hydro-, lithium, (T-4)- (9CI) (CA INDEX NAME)



RN 63717-74-8 HCAPLUS
CN Borate(1-), hydrotriphenyl-, lithium, (T-4)- (9CI) (CA INDEX NAME)

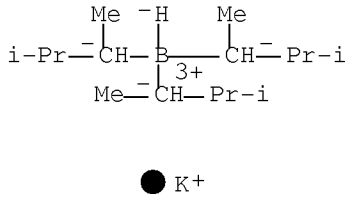


RN 67276-04-4 HCAPLUS
CN Borate(1-), hydrotris(1-methylpropyl)-, sodium (1:1), (T-4)- (CA INDEX NAME)

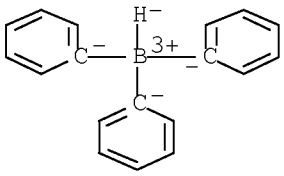


RN 67966-25-0 HCAPLUS
CN Borate(1-), tris(1,2-dimethylpropyl)hydro-, potassium, (T-4)- (9CI) (CA

INDEX NAME)

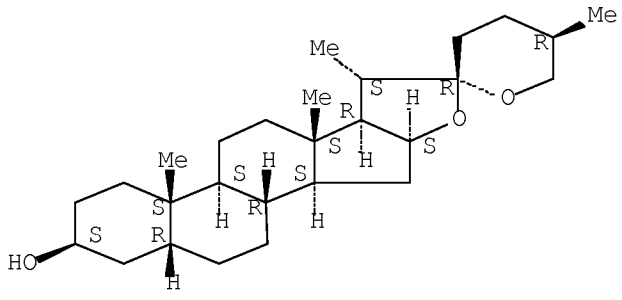


RN 99747-36-1 HCAPLUS
CN Borate(1-), hydrotriphenyl-, potassium, (T-4)- (9CI) (CA INDEX NAME)



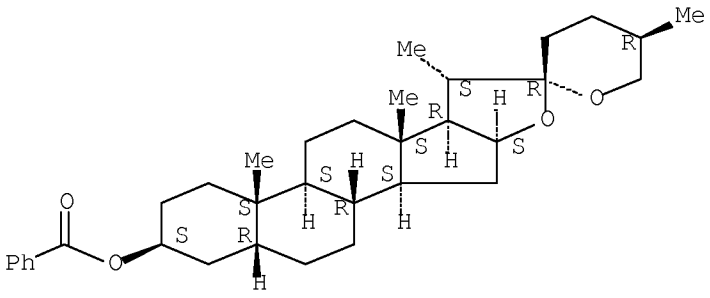
IT 126-18-1P, Smilagenin 4952-69-6P,
Smilagenin benzoate
RL: SPN (Synthetic preparation); PREP (Preparation)
(stereospecific reduction of sapogen-3-ones)
RN 126-18-1 HCAPLUS
CN Spirostan-3-ol, (3β,5β,25R)- (CA INDEX NAME)

Absolute stereochemistry.

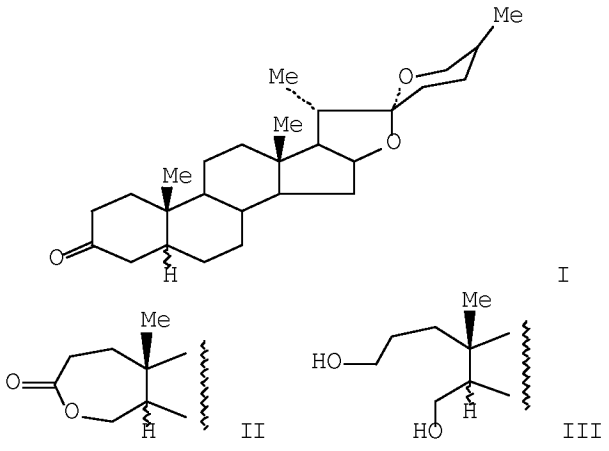


RN 4952-69-6 HCAPLUS
CN Spirostan-3-ol, benzoate, (3β,5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



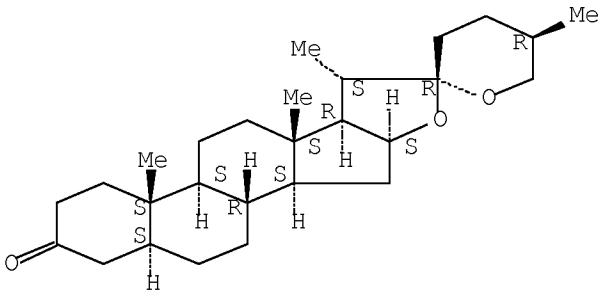
L71 ANSWER 2 OF 4 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1983:405899 HCAPLUS Full-text
DN 99:5899
TI Modified steroids. Communication XII. Study of the Baeyer-Villiger reaction in a series of derivatives of a steroid compound diosgenin
AU Irismetov, M. P.; Goryaev, M. I.; Rustambekova, G. B.; Mirzasalieva, N. A.
CS Inst. Khim. Nauk, Alma-Ata, USSR
SO Izvestiya Akademii Nauk Kazakhskoi SSR, Seriya Khimicheskaya (1983), (1), 75-7
CODEN: IKAKAK; ISSN: 0002-3205
DT Journal
LA Russian
GI



AB Diosgenones I underwent Baeyer-Villiger oxidation by BzO2H in CHCl3 to give lactones II, which were reduced by LiAlH4 to give diols III.
CC 32-8 (Steroids)
ST diosgenone Baeyer Villiger oxidn; homooxaspirostanone lactone prepn redn; secospirostanediol
IT Steroids, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(Baeyer-Villiger oxidation of diosgenins)
IT Oxidation
(Baeyer-Villiger, of diosgenins, homooxaspirostanones from)

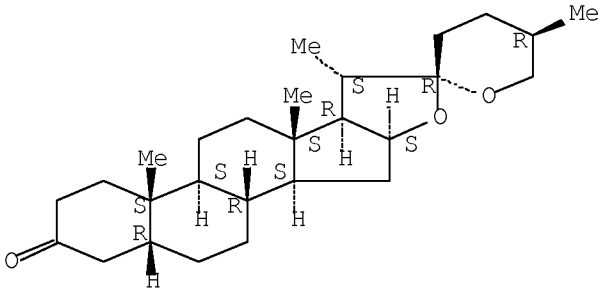
IT 470-07-5 85881-65-8
RL: RCT (Reactant); RACT (Reactant or reagent)
(Baeyer-Villiger oxidation of)
IT 512-07-2P 85853-07-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and reduction-ring cleavage of)
IT 470-07-5
RL: RCT (Reactant); RACT (Reactant or reagent)
(Baeyer-Villiger oxidation of)
RN 470-07-5 HCAPLUS
CN Spirostan-3-one, (5α,25R)- (CA INDEX NAME)

Absolute stereochemistry.



IT 512-07-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and reduction-ring cleavage of)
RN 512-07-2 HCAPLUS
CN Spirostan-3-one, (5β,25R)- (9CI) (CA INDEX NAME)

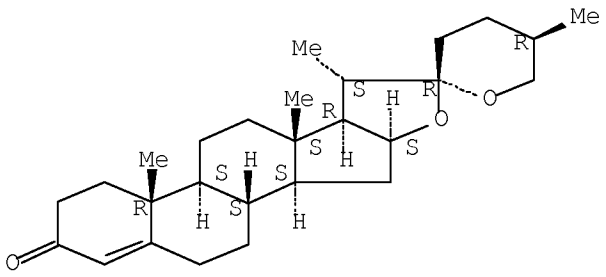
Absolute stereochemistry.



L71 ANSWER 3 OF 4 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1960:74810 HCAPLUS Full-text
DN 54:74810
OREF 54:14301g-h
TI A new method for the preparation of diosgenone
AU Chakravarti, R. N.; Mitra, M. N.; Chakravarti, Debi
CS Bethune Coll., Calcutta

SO Bulletin of the Calcutta School of Tropical Medicine (1959), 7, 145
CODEN: BCSTA4; ISSN: 0068-5372
DT Journal
LA Unavailable
OS CASREACT 54:74810
AB Diosgenone (isospirost-4-en-3-one) was obtained from diosgenin by dissolving the latter (2 g.) in 40 ml. freshly distilled p-cymene and adding 1 g. Raney Ni in a 250- ml. flask fitted with an air condenser. The mixture was refluxed 12 hrs. in an atmospheric of dry N, was filtered hot, and the solvent removed by distillation under reduced pressure at 125-130°. The residue (1.4 g.) was chromatographed over Al2O3, and the crystalline solid eluted with 2:1 petr. ether-C6H6. The product was further purified by recrystn. from alc. The method was applicable to the preparation of 4-cholesten-3-one from cholesterol.
CC 10J (Organic Chemistry: Steroids)
IT Ultraviolet and visible, spectra
(of diosgenin)
IT 601-57-0P, Cholest-4-en-3-one 6870-79-7P, Diosgenone
RL: PREP (Preparation)
(preparation of)
IT 6870-79-7P, Diosgenone
RL: PREP (Preparation)
(preparation of)
RN 6870-79-7 HCAPLUS
CN Spirost-4-en-3-one, (25R)- (CA INDEX NAME)

Absolute stereochemistry.



L71 ANSWER 4 OF 4 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1942:20583 HCAPLUS Full-text
DN 36:20583
OREF 36:3182i,3183a-c
TI Sterols. CXXXIX. Sapogenins. 59. The bio-reduction of 4-dehydrotigogenone
AU Marker, Russell E.; Wittbecker, Emerson L.; Wagner, R. B.; Turner, D. L.
SO Journal of the American Chemical Society (1942), 64, 818-22
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
AB A 20-kg. male dog was fed daily (for 3 consecutive days) a mixture of 300 g. of dog biscuits and 30 g. of lard containing 3 g. of 4-dehydrotigogenone (I) and in addition 1 g. of I in 20 cc. peanut oil was injected subcutaneously; the feces were extracted with Me2CO and ether and the residue from the extract was hydrolyzed with alc. KOH; the nonsaponifiable fraction (9.5 g.) gave 9.5 g. of a digitonin (II) precipitate, which yielded 0.2 g. of diosgenin and 0.1

g. of smilagenin; the fraction not precipitated by II contained 4.2 g. of unchanged I and 0.4 g. of epismilagenin, C29H46O4 (III), m. 217-20° (acetate, m. 158-60°), separated as the succinic ester. III was also prepared from smilagenone by catalytic reduction (PtO2 in EtOH for 75 min. at room temperature) or by the action of Na in absolute EtOH. III is reoxidized to IV by CrO3 in 90% AcOH. Further reduction (PtO2 in AcOH at 70-5° and 3 atmospheric of H for 10 hrs.) gives epidihydrosarsapogenin, m. 134-6°; crystallization from Me2CO gives a polymorphic form, m. 180-2°. The dog normally excretes epicoprosterol in a considerable amount; this lends addnl. support to Schoenheimer's theory (C. A. 32, 7985.2) that cholestenone is an intermediate in the formation of coprosterol in the organism. The significance of these facts is discussed.

CC 10 (Organic Chemistry)

IT Animal organism
(4-dehydrotigogenone reduction in)

IT Reduction
(of 4-dehydrotigogenone in animal organism)

IT Sarsasapogenin, epidihydro-
RL: PREP (Preparation)

IT 6870-79-7, Tigogenone, 4-dehydro-
(bio-reduction of)

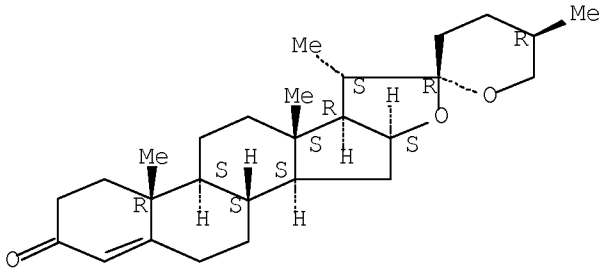
IT 126-18-1P, Smilagenin 512-04-9P, Diosgenin 512-07-2P, Smilagenone 16653-88-6P, Epismilagenin 106759-14-2P, Epismilagenin, acetate
RL: PREP (Preparation)
(preparation of)

IT 6870-79-7, Tigogenone, 4-dehydro-
(bio-reduction of)

RN 6870-79-7 HCAPLUS

CN Spirost-4-en-3-one, (25R)- (CA INDEX NAME)

Absolute stereochemistry.

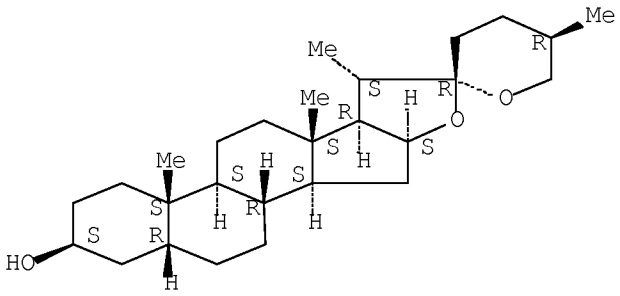


IT 126-18-1P, Smilagenin 512-04-9P, Diosgenin 512-07-2P, Smilagenone 16653-88-6P, Epismilagenin 106759-14-2P, Epismilagenin, acetate
RL: PREP (Preparation)
(preparation of)

RN 126-18-1 HCAPLUS

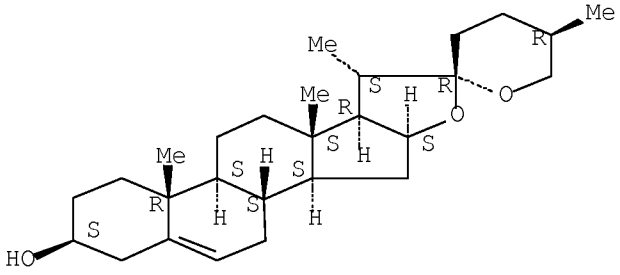
CN Spirostan-3-ol, (3β,5β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



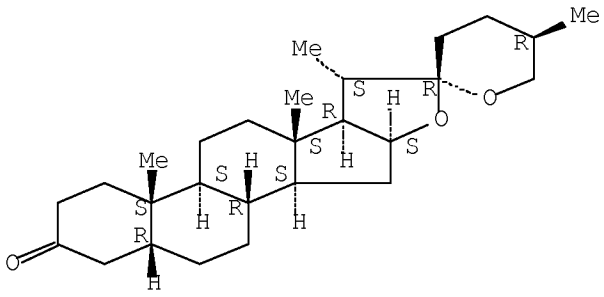
RN 512-04-9 HCAPLUS
CN Spirost-5-en-3-ol, (3β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



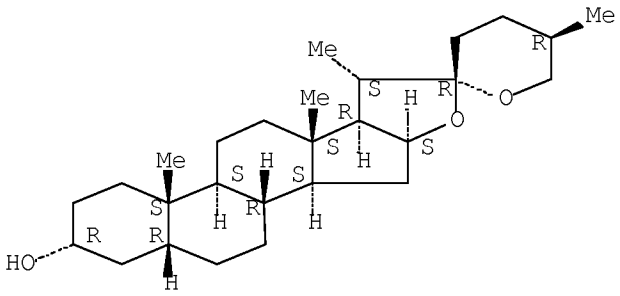
RN 512-07-2 HCAPLUS
CN Spirostan-3-one, (5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



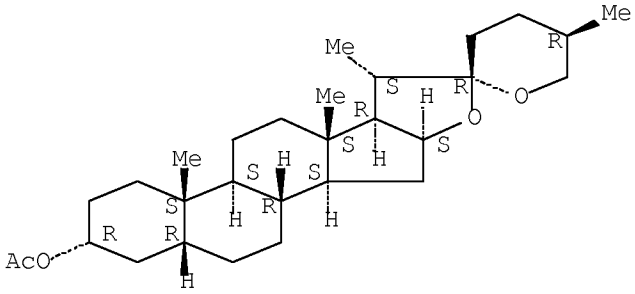
RN 16653-88-6 HCAPLUS
CN Spirostan-3-ol, (3α,5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 106759-14-2 HCAPLUS
CN Spirostan-3-ol, 3-acetate, (3α,5β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



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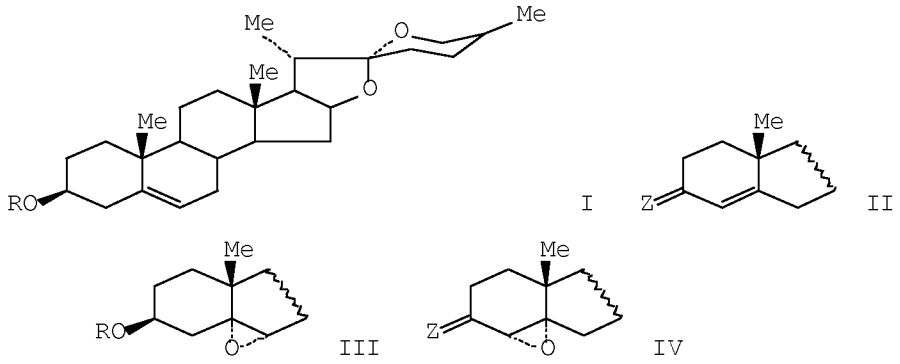
L95 ANSWER 1 OF 1 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1983:215889 HCAPLUS Full-text
DN 98:215889
OREF 98:32841a,32844a
ED Entered STN: 12 May 1984
TI Modified steroids. XI. Preparation of epoxy compounds from diosgenin and its derivatives
AU Irismetov, M. P.; Goryaev, M. I.; Rustembekova, G. B.; Mirzasalieva, N. A.
CS Inst. Khim. Nauk, Alma-Ata, USSR
SO Zhurnal Obshchei Khimii (1983), 53(2), 462-5
CODEN: ZOKHA4; ISSN: 0044-460X
DT Journal
LA Russian
CC 32-8 (Steroids)
GI



AB Epoxidn. of diosgenins I (R = H, Ac) and II (Z = O, H2) by BzOOH in CHCl3 gave epoxides III and IV, resp. LiAlH4 reduction of III (R = H, Ac) and IV (Z = O) gave 5α-spirostane-3β,5-diol.

ST epoxidn diosgenin; epoxyhydroxyspirostane

IT Steroids, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(epoxidn. of diosgenins)

IT Epoxidation
(of diosgenins)

IT 512-04-9 6870-79-7 85707-30-8
RL: RCT (Reactant); RACT (Reactant or reagent)
(epoxidn. of)

IT 85707-31-9P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and acetylation of)

IT 1061-54-7P 3514-60-1P 66965-00-2P 85719-33-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and epoxide ring cleavage of)

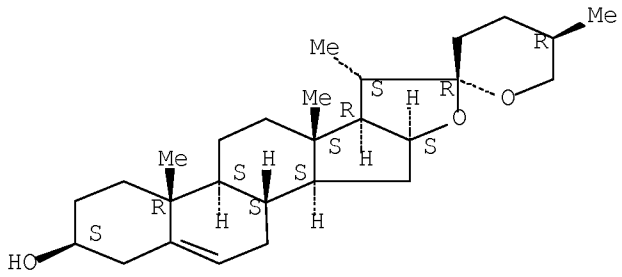
IT 85707-32-0P 85707-33-1P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

IT 512-04-9 6870-79-7
RL: RCT (Reactant); RACT (Reactant or reagent)
(epoxidn. of)

RN 512-04-9 HCAPLUS

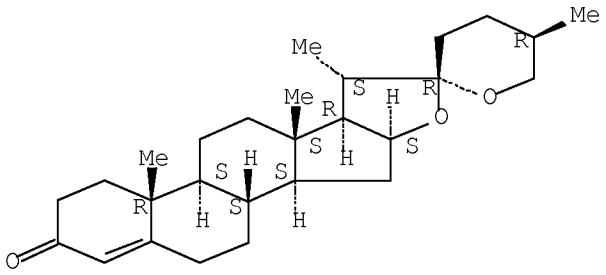
CN Spirost-5-en-3-ol, (3β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



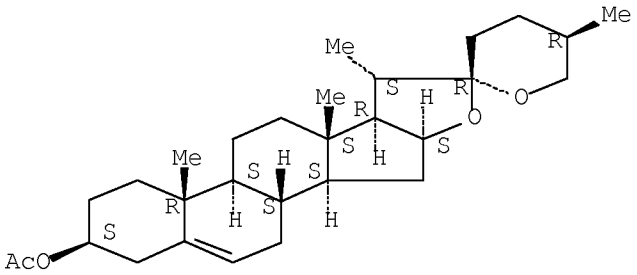
RN 6870-79-7 HCAPLUS
CN Spirost-4-en-3-one, (25R)- (CA INDEX NAME)

Absolute stereochemistry.



IT 1061-54-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and epoxide ring cleavage of)
RN 1061-54-7 HCAPLUS
CN Spirost-5-en-3-ol, acetate, (3β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



=> => d bib abs hitstr retable tot l97

L97 ANSWER 1 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1981:407585 HCAPLUS Full-text
DN 95:7585
OREF 95:1443a,1446a
TI Study of synthetic transformations of a steroidal compound of diosgenin
AU Irismetov, M. P.; Goryaev, M. I.
CS USSR
SO Trudy Instituta Khimicheskikh Nauk, Akademiya Nauk Kazakhskoi SSR (1980), 52, 17-39
CODEN: TIKNAG; ISSN: 0568-5087
DT Journal
LA Russian
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

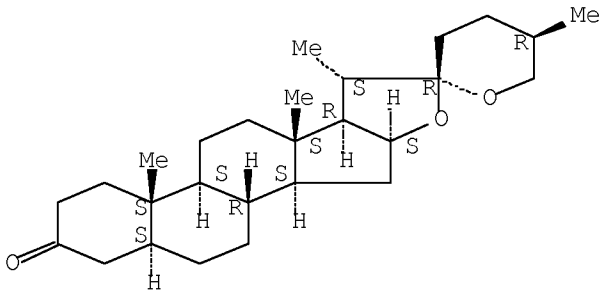
AB Heterocyclic analogs of diosgenin were prepared Thus, cyclocondensation of 2-formyldiosgenone with N2H4 and HONH2 gave the pyrazalodiosgenin I and isoxazolodiosgenin II, resp. Fisher indole synthesis of diosgenone with PhNHNH2 gave indolodiosgenin III, and Beckmann rearrangement of dihydrodiosgenone oxime gave lactams IV and V (Z = O), which were reduced by LiAlH4 to give IV and V (Z = H2). Baeyer-Villiger oxidation of dihydrodiosgenone gave lactam VI, and cyclocondensation of 2α-bromodihydrodiosgenone with PhCH:NNHC(S)NH2 gave the thiazolodiosgenin VII.

IT 470-07-5P 512-07-2P
RL: RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
(Fisher indole synthesis of)

RN 470-07-5 HCAPLUS

CN Spirostan-3-one, (5α,25R)- (CA INDEX NAME)

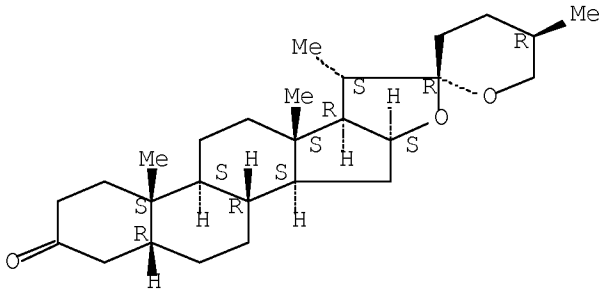
Absolute stereochemistry.



RN 512-07-2 HCAPLUS

CN Spirostan-3-one, (5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

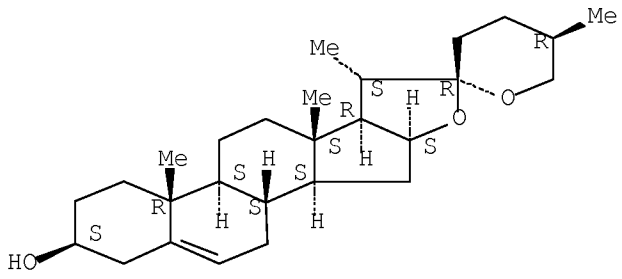


IT 512-04-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(oxidation of)

RN 512-04-9 HCAPLUS

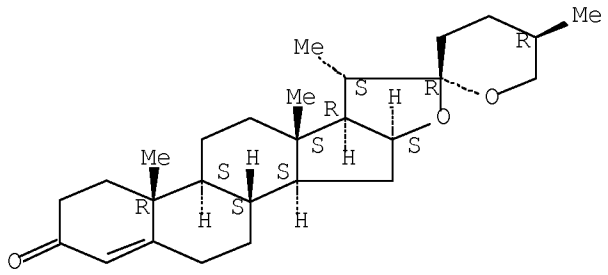
CN Spirost-5-en-3-ol, (3β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



IT 6870-79-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and acylation of)
RN 6870-79-7 HCAPLUS
CN Spirost-4-en-3-one, (25R)- (CA INDEX NAME)

Absolute stereochemistry.



L97 ANSWER 2 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1966:68078 HCAPLUS Full-text
DN 64:68078
OREF 64:12755e-h,12756a-b
TI Structure of yononin. A novel type of spirostanol glycoside
AU Kawasaki, T.; Miyahara, K.
CS Kyushu Univ., Fukuoka, Japan
SO Tetrahedron (1965), 21(12), 3633-9
CODEN: TETRAB; ISSN: 0040-4020
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB cf. CA 59, 15535g. Isolation from the rhizome of Dioscorea tokoro gave yononin (I), and α-L-arabinoside of yonogenin (II) (Takada, et al., CA 53, 16206f). I (200 mg.) in 5 ml. HCONMe2 methylated with 2.3 g. MeI and 1 g. Ag2O, the procedure repeated twice, and the sirup refluxed 2 hrs. with 4 ml. 2N HCl in 50% aqueous alc. gave 24 mg. aglycon (II), m. 184-6°, [α]D -58° (c 0.55, all in CHCl3), Rf 0.34 (3:1 C6H12-EtOAc, 10% H2SO4 spray). II must be a yonogenin monomethyl ether and synthetic 2- and 3-methyl ethers were prepared for comparison. Preparation from diosgenin gave 25D-spirost-4-en-3-one (III), m. 185-6° [α]D 4° (c 0.52). III (5 g.) in 350 ml. MeOH treated 10 min. with 20 ml. 30% H2O2 and 20 ml. 4N NaOH, the mixture stirred 7 hrs. at 2° and kept 16 hrs. at 0° gave 4,5-epoxy-25D-spirostan-3- one, m. 205-7°, [α]D 23° (c

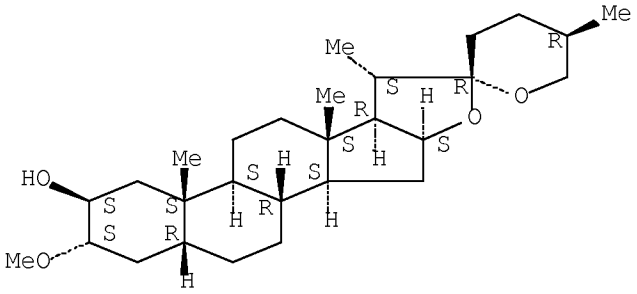
0.53). The epoxide (2.98 g.) in 100 ml. Me2CO treated dropwise with 6 ml. 25% H2SO4 and the mixture kept 4 days at 20° gave the 2α-hydroxy-4-en-3-one (IV), m. 213.5-15.5° [α]D 21° (c 0.65), methylated (1 g.) in 25 ml. dry C6H6 by stirring 20 hrs. with 3 g. MeI and 3 g. Ag2O to give the 2α-methoxy-4-en-3-one (V), m. 198-201°, [α]D 29° (c 0.44). V (200 mg.) in 40 ml. alc. hydrogenated over 50 mg. 10% Pd-C gave 19 mg. 2α-methoxy-25D-spirost-4-en-3-ol, m. 201-2°, [α]D 11° (c 0.44), and 2β-methoxy-25D,5β-spirostan- 3-one (VI), m. 212°. VI (20 mg.) reduced 4 hrs. by stirring in 2 ml. dry C5H5N containing 5 mg. LiBH4 gave 2β-methoxy-25D, 5β-spirostan-3β-ol, m. 205-8°, [α]D -49° (c 0.51), and 2β-methoxy-25D,5β-spirostan-3α-ol, m. 265-6°, [α]D -119° (c 0.37), identical with II 2-methyl ether. III (770 mg.) acetylated overnight at 20° with 20 ml. 1:3 Ac2O-C5H5N gave 740 mg. 2α-acetoxy-4-en-3-one (VII), m. 248-50.5°, [α]D -15° (c 0.66). VII (400 mg.) in 30 ml. EtOAc hydrogenated over 50 mg. 10% Pd-C 10 min. and the crystalline mass (395 mg.) reduced in 50 ml. MeOH with 100 mg. NaBH4, the product (374 mg.) methylated in 15 ml. dry C6H6 with 300 mg. MeI and 500 mg. Ag2O for 40 hrs., and the resultant Me ether acetate refluxed 40 min. with 30 ml. 5% KOH-MeOH gave a mixture of 3-methoxy-25D-spirostan-2-ols. The mixture (340 mg.) chromatographed on 10 g. Al2O3 and eluted with C6H6 gave 248 mg. 3α-methoxy-25D,5β-spirostan-2α-ol (VIII), m. 162-3°, [α]D -31° (c 0.70). VIII (16 mg.) in 1 ml. 90% AcOH oxidized with 0.1 ml. solution (200 mg. CrO3 in 1 ml. 90% AcOH) under stirring 4.5 hrs. gave 10 mg. 3α-methoxy-25D,5β-spirostan- 2-one(IX), m. 198°, [α]314 -741°, [α]280 36° (c 0.305, MeOH). IX (50 mg.) in 5 ml. MeOH treated with NaBH4 gave 42 mg. compound, m. 161 .apprx. 2°. IX (71 mg.) reduced with LiBH4 in C5H5N gave VIII and 3α-methoxy-25D,5β-spirostan- 2β-ol, m. 185 .apprx. 8°, [α]D -58° (c 0.63), identical with II. Consequently, I is defined as O-α-L-arabinosyl- (1-2)-25D,5β-spirostan-2β,3α-diol (yonogenin 2-α-L-arabinoside). This is the 1st spirostanol glycoside shown to have the sugar moiety combined with an OH group other than that at C-3 of the aglycon.

IT 5247-71-2P, 5β,25D-Spirostan-2β-ol, 3α-methoxy-
5247-73-4P, 25D-Spirost-4-en-3-one, 2α-hydroxy-
5247-75-6P, 5β,25D-Spirostan-2α-ol, 3α-methoxy-
5289-76-9P, 5β,25D-Spirostan-3α-ol, 2β-methoxy-
5372-57-6P, 25D-Spirost-4-en-3-one, 2α-methoxy-
5373-18-2P, 5β,25D-Spirostan-3-one, 2β-methoxy-
5605-39-0P, 25D-Spirost-4-en-3-ol, 2α-methoxy-
5605-40-3P, 5β,25D-Spirostan-3β-ol, 2β-methoxy-
6870-79-7P, 25D-Spirost-4-en-3-one
RL: PREP (Preparation)
(preparation of)

RN 5247-71-2 HCAPLUS

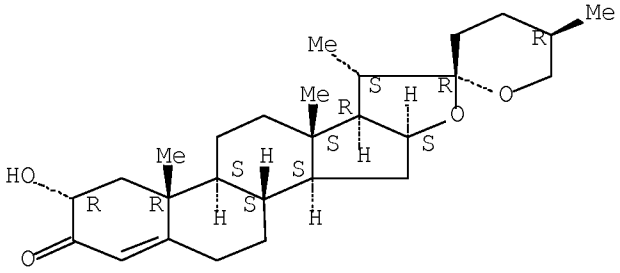
CN Spirostan-2-ol, 3-methoxy-, (2β,3α,5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



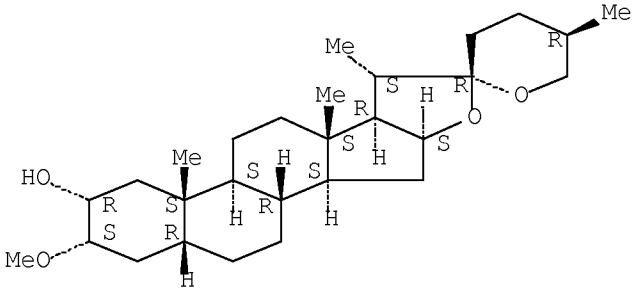
RN 5247-73-4 HCAPLUS
CN 25D-Spirost-4-en-3-one, 2α-hydroxy-, (25R)- (8CI) (CA INDEX NAME)

Absolute stereochemistry.



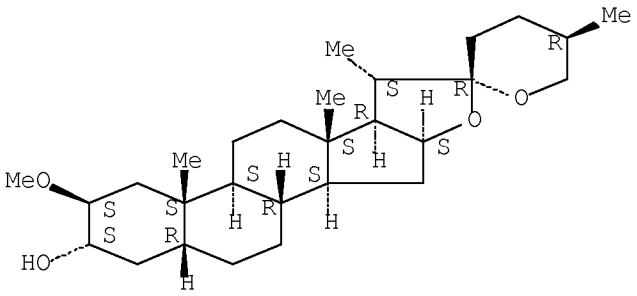
RN 5247-75-6 HCAPLUS
CN 5β,25D-Spirostan-2α-ol, 3α-methoxy-, (25R)- (8CI) (CA INDEX NAME)

Absolute stereochemistry.



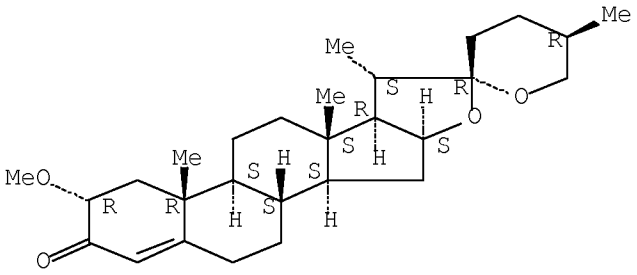
RN 5289-76-9 HCAPLUS
CN 5β,25D-Spirostan-3α-ol, 2β-methoxy-, (25R)- (8CI) (CA INDEX NAME)

Absolute stereochemistry.



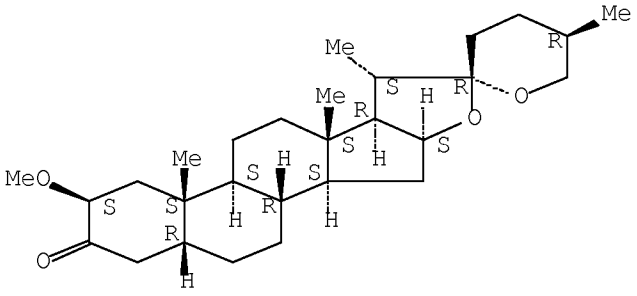
RN 5372-57-6 HCAPLUS
CN Spirost-4-en-3-one, 2-methoxy-, (2α,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



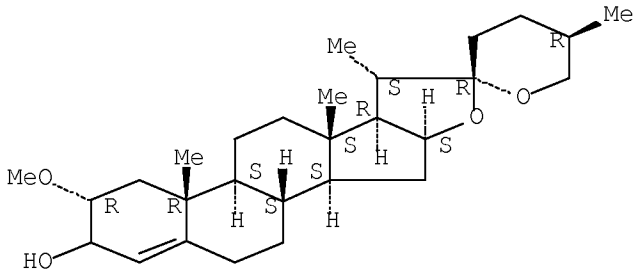
RN 5373-18-2 HCAPLUS
CN 5β,25D-Spirostan-3-one, 2β-methoxy-, (25R)- (8CI) (CA INDEX NAME)

Absolute stereochemistry.



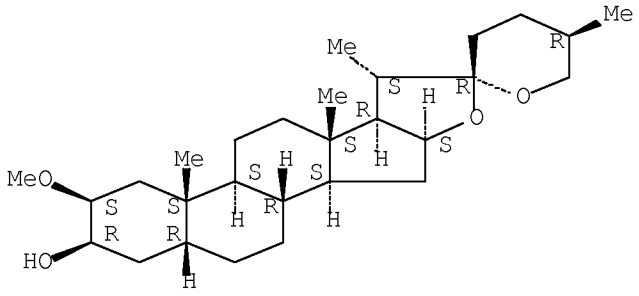
RN 5605-39-0 HCAPLUS
CN 25D-Spirost-4-en-3-ol, 2α-methoxy-, (25R)- (8CI) (CA INDEX NAME)

Absolute stereochemistry.



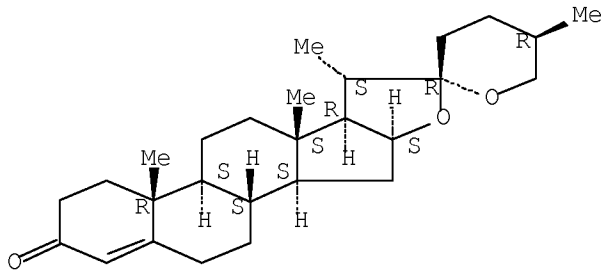
RN 5605-40-3 HCAPLUS
CN Spirostan-3-ol, 2-methoxy-, (2β,3β,5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 6870-79-7 HCAPLUS
CN Spirost-4-en-3-one, (25R)- (CA INDEX NAME)

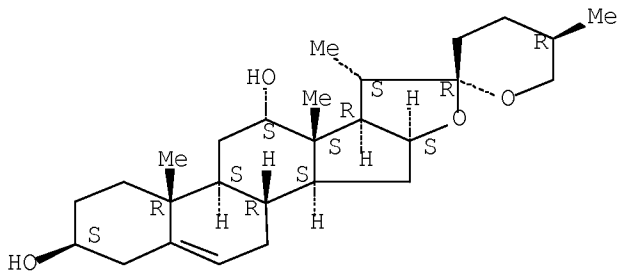
Absolute stereochemistry.



L97 ANSWER 3 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1963:428741 HCAPLUS Full-text
DN 59:28741
OREF 59:5234b-g
TI Steroidal components of domestic plants. XL. Constituents of Heloniopsis orientalis. 3. The structure of heloniogenin
AU Okanishi, Tameto; Akahori, Akira; Yasuda, Fumio
CS Shionogi Co., Osaka, Japan
SO Chemical & Pharmaceutical Bulletin (1962), 10, 1195-9

CODEN: CPBTAL; ISSN: 0009-2363
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. Shionogi Kenkyusho Nempo 11, 97-101(1961); CA 57,8637h. In addition to the properties and derivs. of heloniogenin (I) previously reported [ibid. 10, 1411-15(1960)], its monoacetylation and CrO3 oxidation were described. I (500 mg.) kept with 4 ml. Ac2O in C5H5N 2 hrs. at 10° and the mixture poured into ice H2O, and extracted with ether yielded 572 mg. residue from the extract, which was separated by Al2O3 chromatography into 10 mg. previously reported diacetate, m. 184-5°, 180 mg. unchanged I, m. 212-13°, and 225 mg. desired 3-acetate (II) of I, m. 218-19°, [α]25 -89.6 ± 2° (c 1.029, CHCl3). Oxidation of 280 mg. I with CrO3 in AcOH 30 min. at room temperature yielded 261 mg. mixture, which was separated by Al2O3 chromatography into 21 mg. 25D-spirost-4-ene-3,12-dione (III), m. 248-50°, and 42 mg. gentrogenin (3β-hydroxy-25D-spirost-5-en-12-one) (IV), m. 215-16°, [α]28D -56.0 ± 2° (c 1.021, CHCl3), and 42 mg. mixture of I and IV. Similar oxidation of 450 mg. II yielded 420 mg. mixture, which was separated by Al2O3 chromatography into 240 mg. IV acetate, m. 224-5°, [α]25D -58.1 ± 2° (c 1.016, CHCl3), and 150 mg. recovered II. These results showed I to be 25D-spirost-5-ene-3β,12ξ-diol. The configuration of the 12-OH group remained to be determined IV acetate (300 mg.) reduced with LiAlH4 in ether in the usual way yielded 317 mg. mixture of isomers, separated by Al2O3 chromatography into 165 mg. 3β,12β-diol (V) [acetate (VI) m. 206-7°, [α]27D -117.8 ± 2° (c 1.015, CHCl3)] and 105 mg. 3β,12α-diol (VII), m. 211-12°, [α]23D -89.2 ± 2° (c 1.062, CHCl3); diacetate (VIII) m. 180-2°, [α]27D -61.8 ± 2° (c 1.080, CHCl3). VI (50 mg.) hydrolyzed with KOH-EtOH yielded 45 mg. V, m. 233-5°, [α]27D -116.4 ± 2° (c 0.993, CHCl3). IV acetate (230 mg.) reduced with NaBH4 in EtOH gave similar results and yielded 130) mg. V and 50 mg. VII. V and VI showed the same phys. consts. as isochiapagenin (IX) (m. 236-7°, [α]D -121°) and its acetate (m. 206-7°, [α]D -120°), obtained from chiapagenin by refluxing 94 hrs. with HCl EtOH, and acetylating the resulting IX with Ac2 O-C5H5N. VII and VIII were identical with I and I diacetate, resp., in m.p., [α]D, and infrared spectra, and showed no depression of mixed m.p. The structure of I was thus established as 25D-spirost-5-ene-3β,12α-diol.
IT 6869-16-5, 25D-Spirost-5-ene-3β,12α-diol
(as structure for heloniogenin)
RN 6869-16-5 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12α,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

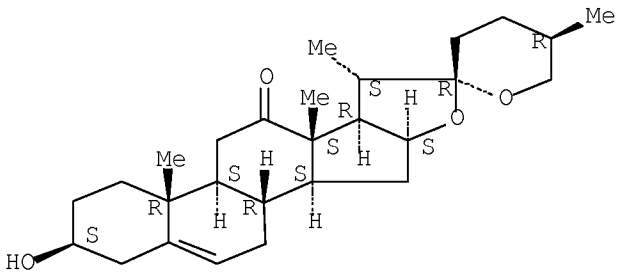


IT 427-28-1P, Gentrogenin 5996-01-0P, Gentrogenin, acetate
6875-60-1P, 25D-Spirost-4-ene-3,12-dione 6877-71-0P,
25D-Spirost-5-ene-3β,12β-diol 59203-51-9P,

Isochiapagenin 103592-10-5P, Heloniogenin, 3-acetate
105063-79-4P, Heloniogenin, diacetate 105859-99-2P,
25D-Spirost-5-ene-3β,12β-diol, diacetate
RL: PREP (Preparation)
(preparation of)

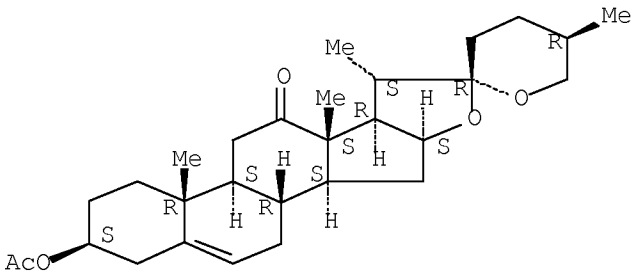
RN 427-28-1 HCAPLUS
CN Spirost-5-en-12-one, 3-hydroxy-, (3β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



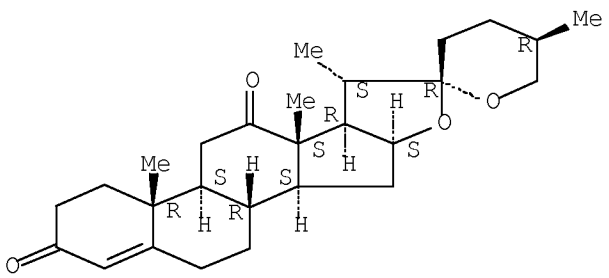
RN 5996-01-0 HCAPLUS
CN Spirost-5-en-12-one, 3-(acetyloxy)-, (3β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



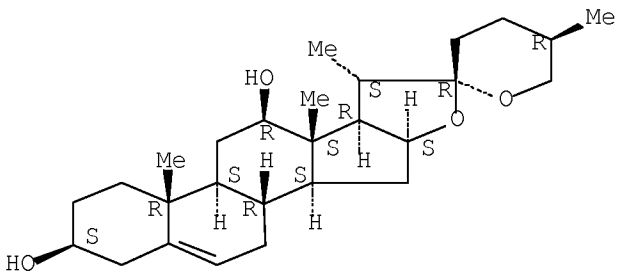
RN 6875-60-1 HCAPLUS
CN Spirost-4-ene-3,12-dione, (25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



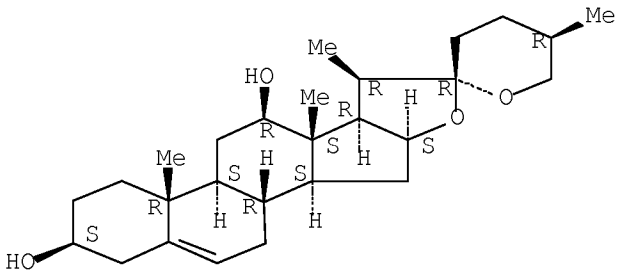
RN 6877-71-0 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



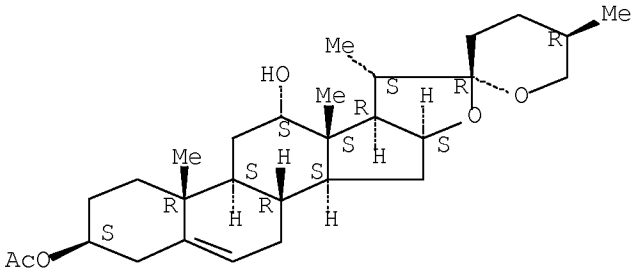
RN 59203-51-9 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12β,20β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



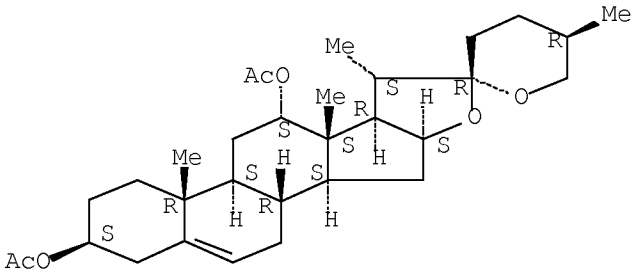
RN 103592-10-5 HCAPLUS
CN Heloniogenin, 3-acetate (7CI) (CA INDEX NAME)

Absolute stereochemistry.



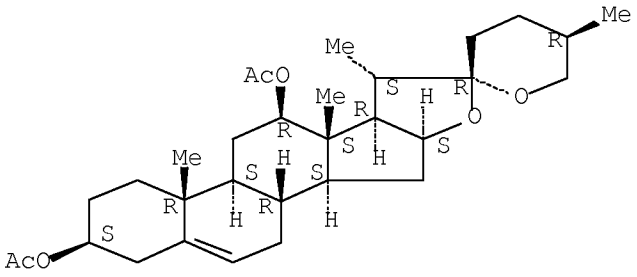
RN 105063-79-4 HCAPLUS
CN Spirost-5-ene-3,12-diol, diacetate, (3β,12α,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



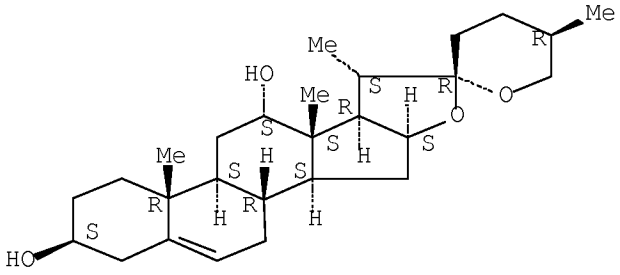
RN 105859-99-2 HCAPLUS
CN 25D-Spirost-5-ene-3β,12β-diol, diacetate (7CI) (CA INDEX NAME)

Absolute stereochemistry.



IT 6869-16-5, Heloniogenin
(structure of)
RN 6869-16-5 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12α,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L97 ANSWER 4 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1962:443009 HCAPLUS Full-text
DN 57:43009
OREF 57:8637h-i,8638a-h
TI Steroidal components of domestic plants. XXXII. Constituents of Reineckia carnea. 4. Structure of kitigenin. 1
AU Sasaki, Kanzo
CS Shionogi & Co., Osaka
SO Chemical & Pharmaceutical Bulletin (1961), 9, 684-92

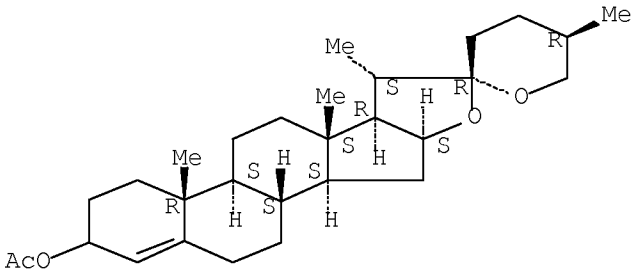
CODEN: CPBTAL; ISSN: 0009-2363
DT Journal
LA Unavailable
OS CASREACT 57:43009
GI For diagram(s), see printed CA Issue.
AB cf. CA 56, 11664a. (Throughout these abstrs. optical rotations were measured in CHCl3). The positions and configurations of 3 of the 4 OH groups of kitigenin (I), previously shown (loc. cit.) to be in ring A, were determined Acetylation of 588 mg. I with Ac2O-C5H5N yielded 724 mg. mixture, separated by CS2 into 370 mg. CS2-insol. diacetate (II), m. 217-19°, [α]29.5D -45.6 ± 2° (c 0.868), and 354 mg. CS2-soluble triacetate (III), m. 219-20.5° (depressed when mixed with II), [α]30D -53.6 ± 2° (c 1.023). II (0.2 g.) in Me2CO treated dropwise with CrO3-H2SO4 yielded 225 mg. ketone (IV), m. 200-2°, [α]24D -64.7 ± 2° (c 1.002). Thus, only 1 OH group in II was oxidized, as evidenced by both ultraviolet and infrared spectra, and the remaining OH group must be tertiary, at C-5. III in C5H5N was dehydrated with SOCl2 to give 74% the 4-ene triacetate (V), m. 218-21° (depressed when mixed with III), [α]24D -129 ± 2° (c 1.105). Infrared bands at 1762 and 1730 cm.-1 confirmed the presence of the enol acetate and acetoxy groups, resp., thus proving an AcO group at C-4. Reductive hydrolysis of 0.1 g. V in tetrahydrofuran with LiAlH4 in ether yielded 81 mg. oxo diol (VI), m. 192-6°, which gave a pos. ketol test with 2,3,5-triphenyltetrazolium chloride, and a neg. FeCl3 color test. VI (48 mg.) oxidized with (AcO)2Cu in AcOH-MeOH yielded 45 mg. 4-hydroxy-1,4-dien-3-one compound (VII), m. 175-95°, which gave a neg. ketol test and a pos. FeCl3 color test, and was acetylated with Ac2O-C5H5N to yield 15 mg. 4-acetoxy-1,4-dien-3-one compound (VIII), m. 212-15°. VII (46 mg.) was also formed by refluxing 62 mg. VI with 3% NaOH-MeOH. Catalytic reduction (Pd-C) of VII in AcOEt gave 4-hydroxy-25D-spirost-4-en-3-one (IX), m. 215-19°, [α]29D 10.3 ± 6° (c 0.361). The structure of IX was confirmed by its synthesis from 0.4 g. diosgenone (X) by oxidation with H2O2 in the presence of OsO4 in ether, whereby 287 mg. X was recovered and 20 mg. IX obtained, identical with the preceding sample. The yield of IX was increased to 30% by increasing the reaction time from 24 to 90 hrs. These results indicated the location of 3 of the 4 OH groups at the 3-, 4-, and 5-positions in I. The configuration of the OH group at C-3 was next determined II (0.2 g.) in C5H5N kept overnight at 0° with MeSO2Cl yielded 98 mg. unsatd. triol diacetate (XI), m. 236-40°, which (22 mg.) was hydrolyzed with 1.5% NaOH-MeOH to yield 20 mg. unsatd. triol (XII), m. 235-9°, [α]24D 18.7 ± 4° (c 0.503). XI (0.2 g.) catalytically hydrogenated (PtO2) in AcOH yielded 196 mg. mixture, separated by Al2O3 chromatography into a trace of (probably) the 4,5-diol monoacetate, m. 195-212°, and 140 mg. corresponding saturated triol diacetate (XIII), m. 204-6°, [α]23D -21.1 ± 2° (c 0.848). X (5 g.) reduced with LiAlH4 in ether yielded 5.02 crude epimeric mixture of 4-en-3-ols, which (1.08 g.) was separated by digitonin precipitation into the 4-en-3α-ol (XIV), m. 182-4°, [α]20D -5.1 ± 3° (c 0.831), and the 4-en-3β-ol (XV), m. 155-7°, [α]23D -39.6 ± 3° (c 0.727) in a 2.5:1 ratio. Acetylation of XIV and XV with Ac2O-C5H5N gave the corresponding 4-en-3α-acetate (XVI), m. 170-2°, [α]18D 89.3 ± 2° (c 1.035), and the 4-en-3β-acetate (XVII), m. 167-9°, [α]22D -82.0 ± 2° (c 1.019). The [M]D differences between the alcs. and their acetates, when compared with those of cholest-4-en-3-ols and their acetates, supported the assigned configurations. cis-Hydroxylation of 1.01 g. XV with OsO4 yielded 0.86 g. mixture separated into 508 mg. C6H6-soluble fraction (A) and 376 mg. C6H6-insol. fraction (B). Chromatography of A over Florisil gave 332 mg. recovered XV and 97 mg. triol mixture, which with B was acetylated with Ac2O-C5H5N to yield 540 mg. acetate mixture, and this chromatographed over Al2O3 yielded 27 mg. 3β,4β,5β-triol 3,4-diacetate, m. 200-3° (identical by mixed m.p. and infrared spectra with XIII obtained indirectly from I), and 425 mg. 3β,4α,5α-triol 3,4-diacetate (XVIII), m. 245.5-6.0°, [α]23D -23.4 ± 2° (c 0.603).

Infrared data were reported in support of the structures of II-IX and XI-XVIII. Thus was established the β-orientation of the 3-OH group, and the cis-relation of the 4- and 5-OH groups.

IT 104759-91-3 107297-14-3 107656-53-1
107741-57-1
(Derived from data in the 7th Collective Formula Index (1962-1966))

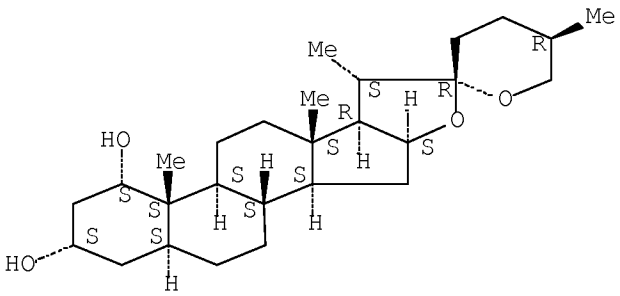
RN 104759-91-3 HCAPLUS
CN 25D-Spirost-4-en-3-ol, acetate (7CI) (CA INDEX NAME)

Absolute stereochemistry.



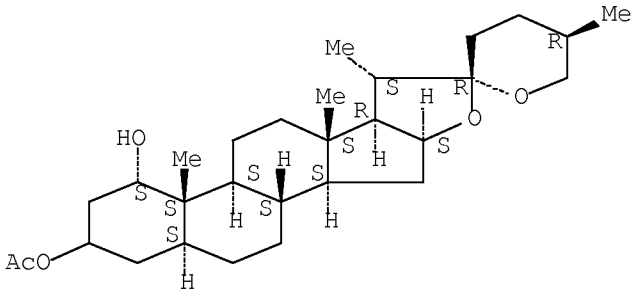
RN 107297-14-3 HCAPLUS
CN 5α,25D-Spirostan-1α,3α-diol (7CI) (CA INDEX NAME)

Absolute stereochemistry.



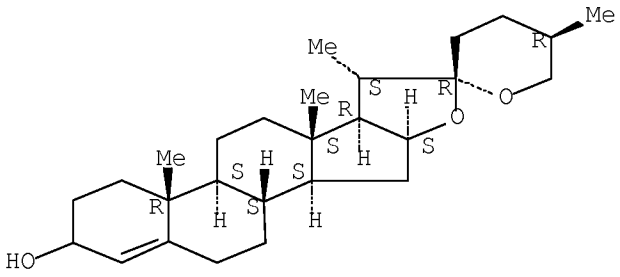
RN 107656-53-1 HCAPLUS
CN 5α,25D-Spirostan-1α,3-diol, 3-acetate (7CI) (CA INDEX NAME)

Absolute stereochemistry.



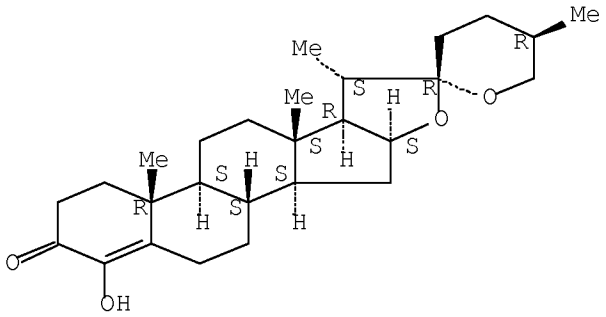
RN 107741-57-1 HCAPLUS
CN 25D-Spirost-4-en-3-ol (7CI) (CA INDEX NAME)

Absolute stereochemistry.



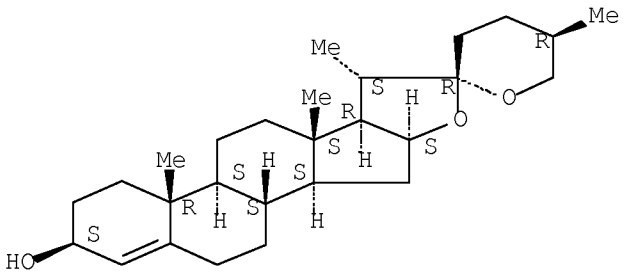
IT 13944-32-6P, 25D-Spirost-4-en-3-one, 4-hydroxy-
16653-41-1P, 25D-Spirost-4-en-3β-ol 16653-54-6P,
25D-Spirost-4-en-3β-ol, acetate 106505-71-9P,
25D-Spirosta-1,4-dien-3-one, 4-hydroxy-
RL: PREP (Preparation)
(preparation of)
RN 13944-32-6 HCAPLUS
CN Spirost-4-en-3-one, 4-hydroxy-, (25R)- (8CI, 9CI) (CA INDEX NAME)

Absolute stereochemistry.



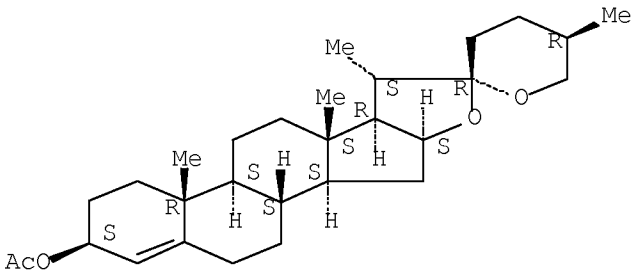
RN 16653-41-1 HCAPLUS
CN Spirost-4-en-3-ol, (3β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



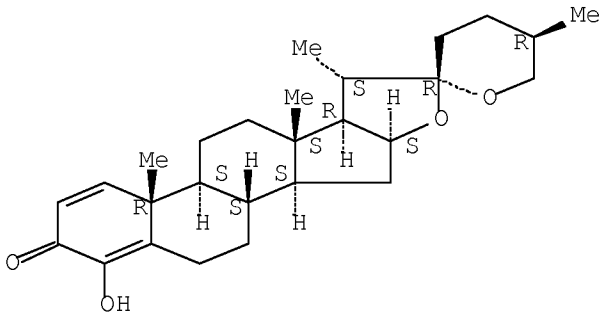
RN 16653-54-6 HCAPLUS
CN Spirost-4-en-3β-ol, acetate, (25R)- (8CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 106505-71-9 HCAPLUS
CN 25D-Spirosta-1,4-dien-3-one, 4-hydroxy- (7CI) (CA INDEX NAME)

Absolute stereochemistry.



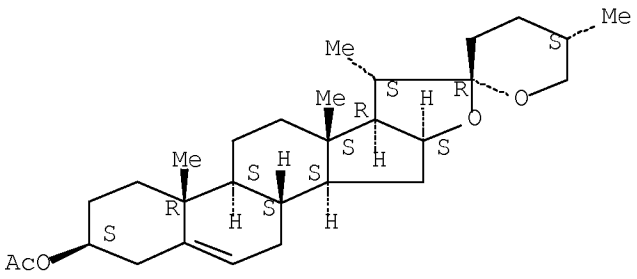
L97 ANSWER 5 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1961:106030 HCAPLUS Full-text
DN 55:106030
OREF 55:19989b-i,19990a-b
TI Chiapagenin and isochiapagenin. Two new steroidal sapogenins from Dioscorea chiapasensis
AU Harrison, I. T.; Velasco, M.; Djerassi, Carl
CS Stanford Univ., Stanford, CA
SO Journal of Organic Chemistry (1961), 26, 155-8
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA Unavailable
AB Two new dihydroxy sapogenins, chiapagenin (I) and isochiapagenin (II), isolated from D. chiapasensis, were shown by appropriate interconversions to be 12β-hydroxyyamogenin and 12β-hydroxydiosgenin, resp. Dried and powdered roots (1 kg.) refluxed 2 hrs. in 10 l. denatured alc., the extraction repeated twice, and the combined exts. concentrated to 5 l., refluxed 4 hrs. with 1.5 l. concentrated HCl, diluted with 30 l. ice H2O and the washed precipitate dried in vacuo at 80° gave 52 g. sapogenins. The product (25 g.) and 4.0 g. Girard reagent T refluxed 1 hr. in 165 ml. 10:1 alc.-AcOH, the cooled solution added to excess saturated aqueous NaHCO3 and unchanged sapogenins (III) (23.5

g.) removed by 3-fold extraction with Et2O, the aqueous layer adjusted to pH 1.0 with concentrated HCl and heated 1 hr. on a steam bath, the cooled mixture extracted with Et2O and the residue on evaporation chromatographed on 60 g. Al2O3 (activity III), eluted with C6H6 and the fraction crystallized from alc., acetylated, and recrystd. from Et2O-C6H14 gave 13 mg. correlogenin (IV) acetate, m. 211-12°. III (8.8 g.) chromatographed on 350 g. Al2O3, eluted with 500 ml. C6H6 and the fraction crystallized from alc. gave 0.46 g. I 3,5-diene derivative, m. 194-5°, [α]D -188° (c 1.1), λ 227, 235, 242 mμ, produced by dehydration during the acid hydrolysis. Further elution with 8:2 C6H6-Et2O gave 1.78 g. yamogenin (V) and diosgenin (VI) mixture, m. 180-7°. The acetylated mixture (2.1 g.) chromatographed on 80 g. Al2O3 (activity II) and eluted with 1:1 C6H6-C6H14 gave 110 mg. material, m. 179-84°, rechromatographed and recrystd. to yield 21 mg. pure VI acetate, m. 196-7°, [α]D -126°, and 370 mg. material, m. 174-6°, recrystd. from alc. to give 219 mg. V acetate, m. 177-8°, [α]D -126°, hydrolyzed to V, m. 195-6°. Further elution of the column with 6:4 C6H6-Et2O gave 4.03 g. fraction, recrystd. from alc. to yield 3.8 g. material, m. 204-5°, converted to the diacetate, m. 194-6° (alc.), [α]D -128° (c 1.9), hydrolyzed to give pure I, m. 257-9°, [α]D -130° (c 1.2), v 922, 895, 853 cm.-1 (CS2), indicative of the neo rather than the iso side chain configuration. I (450 mg.) and 3.1 ml. cyclohexanone in 20 ml. PhMe distilled with passage of some solvent and the mixture refluxed gently 4 hrs. with addition of 315 mg. Al(OCHMe2)3 in 2 ml. PhMe, diluted with H2O and extracted with Et2O gave 190 mg. ketone (VII), m. 214-17° (C6H6-C6H14), [α]D -13° (c 1.0), λ 240 mμ (ε 16,800, alc.). I (480 mg.) kept 2 hrs. at 20° in 4 ml. Ac2O and 25 ml. C5H5N, the monoacetate taken up in 5 ml. Et2O, filtered and the Et2O-soluble fraction chromatographed on 20 g. Al2O3 (activity I), eluted with 4:1 C6H6-Et2O and recrystd. from aqueous MeOH yielded 325 mg. I 3-monoacetate (VIII), m. 176-7°, [α]D -119° (c 0.4). VIII (213 mg.) in 10 ml. AcOH at 10° kept 30 min. with 53 mg. CrO3 in 25 ml. AcOH, diluted with H2O and Et2O, the washed and dried organic phase evaporated and the residue crystallized from dilute MeOH gave 151 mg. IV acetate. I diacetate (2.17 g.) in 50 ml. AcOH hydrogenated 2 hrs. with 100 mg. prereduced PtO2 and the reduction product chromatographed on 100 g. Al2O3 gave dihydrochiapagenin diacetate (IX), m. 204-5°, [α]D -76° (c 0.6), saponified with boiling 5% KOH in MeOH to dihydrochiapagenin (X), m. 202-4° (dilute MeOH), [α]D -79° (c 1.1). IX (33 mg.) and 11.5 g. LiOH.H2O in 40 ml. 80% alc. kept 22 hrs. at 21°, diluted with H2O and extracted with Et2O gave dihydrochiapagenin 12-monoacetate (XI), m. 213-14° (C6H6-C6H14), [α]D -84° (c 0.3). Sisalagenin acetate (109 mg.) refluxed 2 hrs. in absolute alc. with 13 mg. NaBH4, the mixture refluxed 1 hr. with 100 mg. NaOH, diluted with H2O and extracted with Et2O gave X, m. 204-5° (dilute MeOH), [α]D -73° (c 0.7), m. 194-6° (polymorphic form), acetylated and recrystd. from MeOH to give IX. Selective saponification of IX with LiOH.H2O gave XI. A new and larger batch of D. chiapasensis (7 kg.) was extracted to yield 67 g. crystalline and 63 g. oily sapogenin mixture Chromatography of the crystalline fraction gave 13 g. V-VI mixture and 22 g. I. Similar chromatography of the oily fraction produced 20 g. I 3,5-diene derivative, 14 g. V-VI mixture and, after acetylation, 0.535 g. II 3,12-diacetate, m. 206-7° (C6H14), [α]D -120° (c 1.3), saponified in boiling 5% alc. NaOH and recrystd. from MeOH to yield II, m. 236-7°, [α]23D -121° (c 0.8), monoacetylated (101 mg.) to yield 60 mg. II 3-monoacetate, m. 208-10° (C6H14). Oxidation of 50 mg. monoacetate with 15 mg. CrO3 gave 31 mg. botogenin acetate, m. 226-7°, [α]D -56° (c 0.88), reduced (97 mg.) in 10 ml. absolute alc. with 13 mg. NaBH4 by refluxing 2 hrs. and acetylated to yield II acetate, m. 206-7°.

IT 1180-12-7 118923-52-7 119008-69-4
119719-99-2 120576-49-0 121009-56-1
125590-14-9
(Derived from data in the 6th Collective Formula Index (1957-1961))

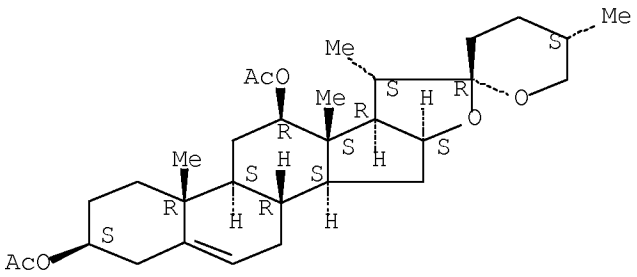
RN 1180-12-7 HCAPLUS
CN Spirost-5-en-3-ol, acetate, (3β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



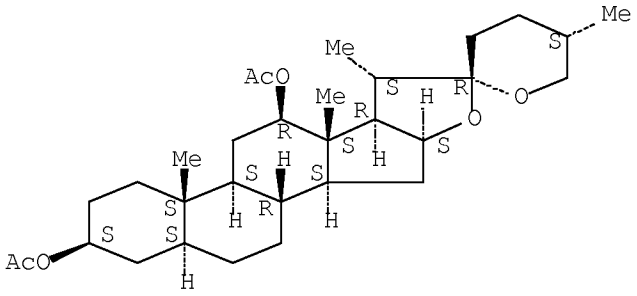
RN 118923-52-7 HCAPLUS
CN 25L-Spirost-5-ene-3β,12β-diol, diacetate (6CI) (CA INDEX NAME)

Absolute stereochemistry.



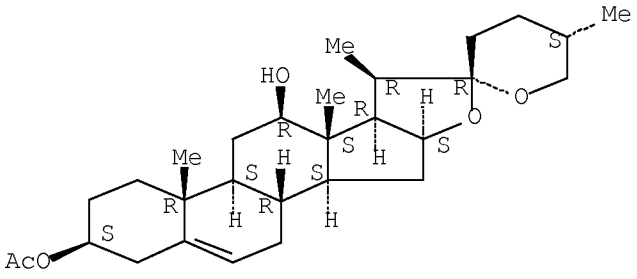
RN 119008-69-4 HCAPLUS
CN 5α,25L-Spirostan-3β,12β-diol, diacetate (6CI) (CA INDEX NAME)

Absolute stereochemistry.



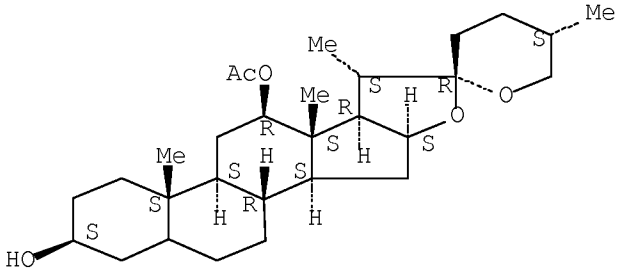
RN 119719-99-2 HCAPLUS
CN Isochiapagenin, 3-acetate (6CI) (CA INDEX NAME)

Absolute stereochemistry.



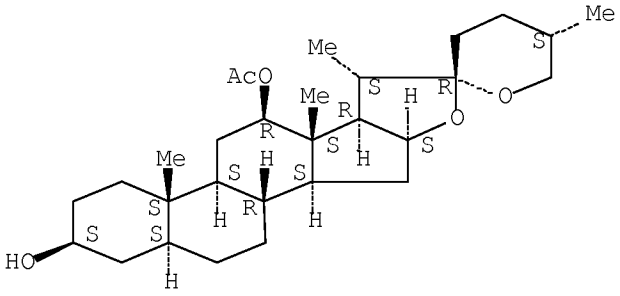
RN 120576-49-0 HCAPLUS
CN Spirostan-3,12-diol, 12-acetate, (3β,12β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



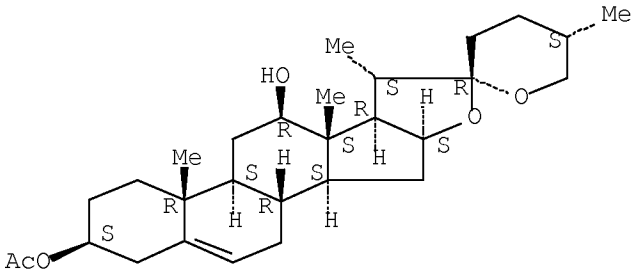
RN 121009-56-1 HCAPLUS
CN 5α,25L-Spirostan-3β,12β-diol, 12-acetate (6CI) (CA INDEX NAME)

Absolute stereochemistry.



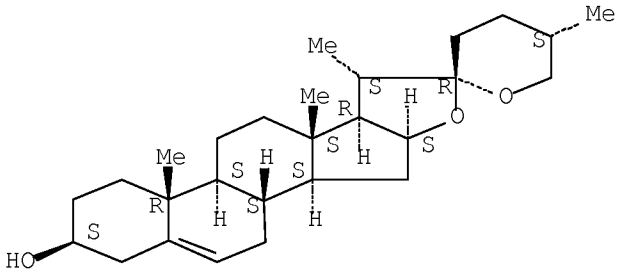
RN 125590-14-9 HCAPLUS
CN Chiapagenin, 3-acetate (6CI) (CA INDEX NAME)

Absolute stereochemistry.



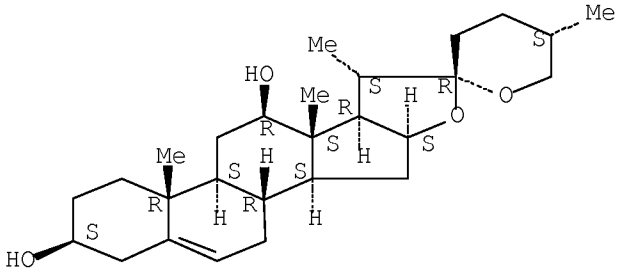
IT 512-06-1P, Yamogenin
RL: PREP (Preparation)
(acetate and separation of yamogenin, from Dioscorea chiapasensis)
RN 512-06-1 HCAPLUS
CN Spirost-5-en-3-ol, (3β,25S)- (CA INDEX NAME)

Absolute stereochemistry.



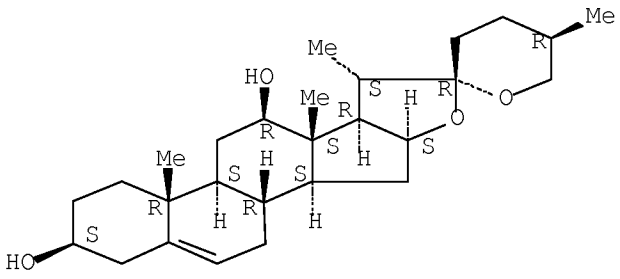
IT 6869-59-6, 25L-Spirost-5-ene-3β,12β-diol
(as chiapagenin structure)
RN 6869-59-6 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



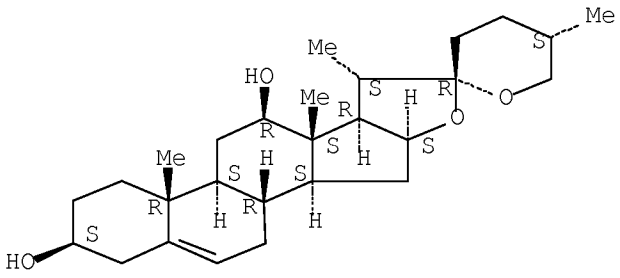
IT 6877-71-0, Diosgenin, 12β-hydroxy-
(as isochiapagenin structure)
RN 6877-71-0 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



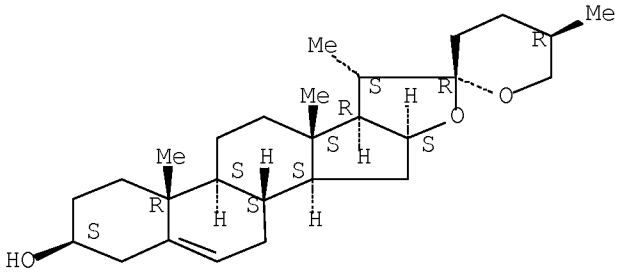
IT 6869-59-6P, Chiapagenin
RL: PREP (Preparation)
(derivs., and separation from Dioscorea chiapasensis)
RN 6869-59-6 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



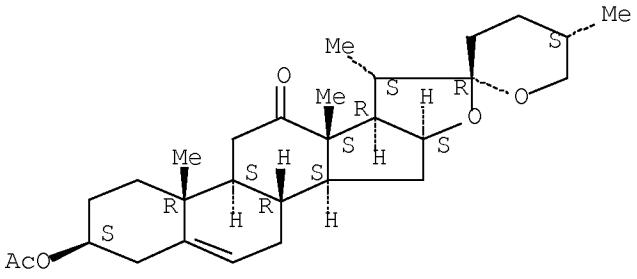
IT 512-04-9, Diosgenin 121193-55-3, Correllogenin, acetate
(from Dioscorea chiapasensis)
RN 512-04-9 HCAPLUS
CN Spirost-5-en-3-ol, (3β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



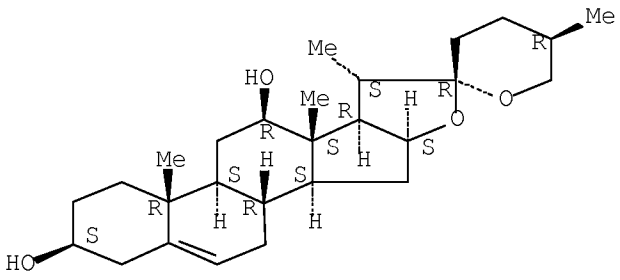
RN 121193-55-3 HCAPLUS
CN 21α,22α,25L-Spirost-5-en-12-one, 3β-hydroxy-, acetate
(6CI) (CA INDEX NAME)

Absolute stereochemistry.



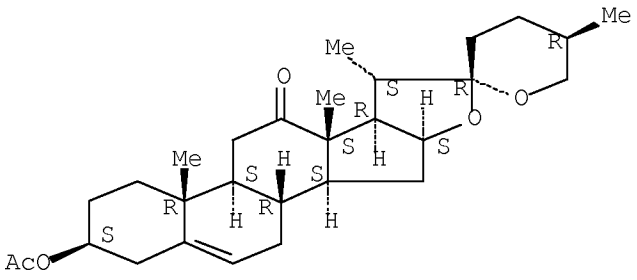
IT 6877-71-0, Yamogenin, 12β-hydroxy-
(identity with chiapagenin)
RN 6877-71-0 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



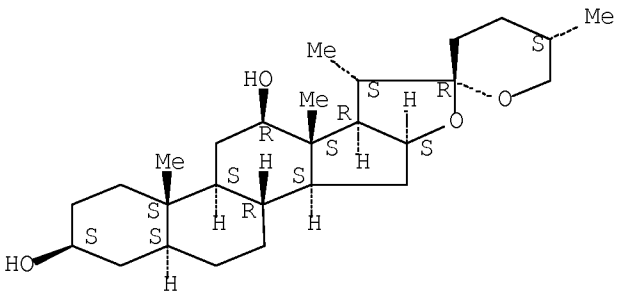
IT 5996-01-0P, Botogenin, acetate 90457-38-8P,
5α,25L-Spirostan-3β,12β-diol 122677-90-1P,
25L-Spirost-4-en-3-one, 12β-hydroxy-
RL: PREP (Preparation)
(preparation of)
RN 5996-01-0 HCAPLUS
CN Spirost-5-en-12-one, 3-(acetyloxy)-, (3β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



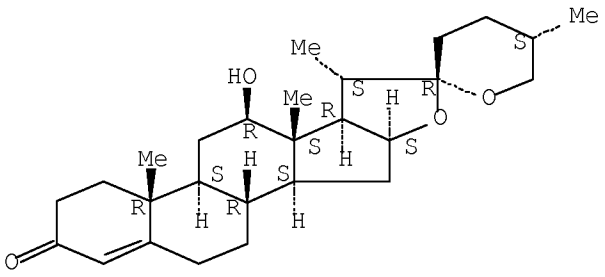
RN 90457-38-8 HCAPLUS
CN Spirostan-3,12-diol, (3β,5α,12β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



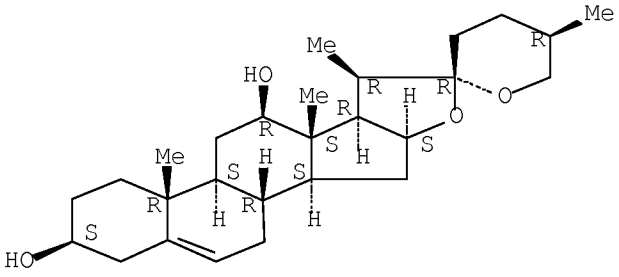
RN 122677-90-1 HCAPLUS
CN 25L-Spirost-4-en-3-one, 12β-hydroxy- (6CI) (CA INDEX NAME)

Absolute stereochemistry.



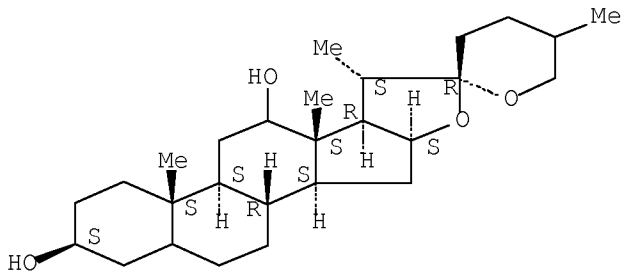
IT 59203-51-9P, Isochiapagenin
RL: PREP (Preparation)
(separation from Dioscorea chiapasensis, and its structure)
RN 59203-51-9 HCAPLUS
CN Spirost-5-ene-3,12-diol, (3β,12β,20β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



IT 892496-15-0, Chiapagenin, dihydro-
(strucure of)
RN 892496-15-0 HCAPLUS
CN INDEX NAME NOT YET ASSIGNED

Absolute stereochemistry.



L97 ANSWER 6 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1961:43404 HCAPLUS Full-text
DN 55:43404
OREF 55:8460a-i,8461a-i,8462a-i,8463a-i,8464a-b
TI The synthesis of the steroidal sapogenins
AU Mazur, Yehuda; Danieli, Naftali; Sondheimer, Franz
CS Weizmann Inst. Sci., Rehovoth, Israel
SO Journal of the American Chemical Society (1960), 82, 5889-908
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
OS CASREACT 55:43404
GI For diagram(s), see printed CA Issue.
AB Isoandrosterone (I) was converted by an 18-stage process to a mixture of tigogenin (II) and neotigogenin (III). I treated with CH2:CMeOAc and H2SO4, the resulting 16-androstene-3β,17-diol diacetate, 90%, m. 170-2°, treated with excess BzO2H, and the crude epoxide treated 0.5 hr. with HClO4 in AcOH at room temperature gave 60% 3β,16α- diacetoxyandrostan-17-one (IV), m. 183-5°, [α]D 56° (all rotations in CHCl3 unless noted otherwise). Activated granulated Zn (15 g.), 10 g. IV, and 100 cc. dry C6H6 heated to remove about 20 cc. C6H6, cooled, treated with 40 g. MeCHBrCO2Et (V), the mixture heated a short time, refluxed 0.5 hr., decanted, the solution worked up, the residual yellow oil refluxed 3 hrs. in 200 cc. MeOH with 12 g. KOH in 10 cc. H2O, diluted with H2O, washed with Et2O, acidified with dilute HCl, extracted with EtOAc, and the extract evaporated gave 3.5 g. 3β,16α,17β-trihydroxy-17- isobisnor-5α-cholanic acid (VI), m. 242-3° (MeOH), [α]D -10° (dioxane). VI in CH2Cl2 treated 16 hrs. at 0° with CH2N2-Et2O gave Me ester (VII) of VI, m. 227-8° (Me2CO-hexane), [α]D -8° (dioxane). VI treated 16 hrs. at room temperature with Ac2O-C5H5N and heated 0.5 hr. at 90° with a little H2O yielded 3,16-diacetate (VIII) of VI, m. 185-6° (MeOH), [α]D -46° (dioxane). Acetylation of VII and treatment of VIII with CH2N2Et2O gave the Me ester of VIII, m. 172-3° (MeOH), [α]D -37°. IV condensed in the usual manner with V and the product chromatographed on 500 g. Al2O3 yielded 0.72 g. Et 3β,16α-diacetoxy-17β-hydroxy-17-isonor-5α-cholanate (IX), m. 177-8° (Et2O-hexane), [α]D -38°, 0.35 g. 3β-acetoxy-16α,17β-dihydroxy-17-isonor-5α-cholanic 22 → 16-lactone (X), m. 220-2° (MeOH), [α]D -55°, 3.92 g. 16α-OH analog (XI) of IX, m. 167-8° (Me2CO-hexane), [α]D -14°, 0.42 g. 3β-OH analog (XII) of IX, m. 154-5° (Me2CO-hexane), and 2.45 g. 3β,16α-di-OH analog (XIII) of IX, m. 201-3° (Me2CO), [α]D -5°. Acetylation of XI, XII, and XIII gave IX, m. 176-8°. VIII (200 mg.) in 50 cc. dry Et2O and 2 cc. SOCl2 kept 2 hrs., evaporated in vacuo, and the residue refluxed 30 min. with 10 cc. absolute EtOH yielded 115 mg. IX, m. 176-7° (Et2O-hexane). IX (200 mg.) in 2:1 pentane-C6H6 chromatographed on 10 g.

Al2O3 yielded 55 mg. unchanged IX and 125 mg. XI, m. 165-7°. XII gave similarly 60% XIII, m. 200-2°, but X, XI, and XIII were recovered unchanged under the same conditions. VI (100 mg.) in 25 cc. Ac2O refluxed 2 hrs., evaporated in vacuo, the residue boiled 15 min. with H2O, and the product isolated with Et2O gave 62 mg. X, m. 218-20° (MeOH), [α]D -56°. VI (100 mg.) in 20 cc. glacial AcOH treated 1 hr. at room temperature with dry HCl, the mixture poured into iced H2O, and the product isolated with Et2O gave 46 mg. X. VIII (100 mg.) and 200 mg. KHSO4 heated 10 min. at 170°/about 1 mm. yielded 62 mg. X. X (200 mg.) and 1.5 g. KOH in 50 cc. 95% MeOH refluxed 2 hrs., treated with H2O and Et2O, the aqueous phase acidified with dilute HCl, extracted with EtOAc, the extract washed (aqueous Na2CO3 and H2O), evaporated, and the residual 3-OH analog (31 mg.) of X acetylated gave X; the aqueous alkaline washing acidified with HCl and the product isolated with EtOAc gave 137 mg. VI, m. 240-2° (Me2CO). IV (20 g.) condensed in the usual manner with 80 g. V, the crude product treated 16 hrs. at room temperature with 50 cc. Ac2O and 50 cc. C5H5N, the product isolated with Et2O, and chromatographed on 750 g. Al2O3 yielded 3.8 g. IX, m. 177-8° (Et2O-hexane), and 11.3 g. XI, which acetylated gave 12.1 g. IX. 3β,17β-Diacetoxyandrostan-16-one (2.5 g.), m. 180-1°, [α]D -118°, treated with 4 g. activated Zn and 10 g. V in 25 cc. C6H6 and the product chromatographed on 100 g. Al2O3 gave 0.91 g. 3-acetate of 3β,16,17β-trihydroxy-16- [1-(carbethoxy)ethyl] androstane isomer A (XIV), m. 188-9° [α]D 5°, (diacetate m. 174-5°, [α]D2°), and 0.42 g. 3-acetate of isomer B, m. 123-4°, [α]D -3° (diacetate m. 125-6°, [α]D -14°). VIII (200 mg.), 5 cc. SOCl2, and 5 cc. dry C6H6 refluxed 2 hrs., evaporated, the residue dissolved in 5 cc. C6H6, the solution added under N to Me2Cd from 620 mg. MeI, 100 mg. Mg, 10 cc. Et2O, and 100 mg. CdCl2, the mixture stirred 2 hrs. under N at room temperature, kept 16 hrs., worked up, and the crude product chromatographed on 12 g. Al2O3 yielded 82 mg. 3β, 16α-diacetoxy-17β-hydroxy-17-isobisnor-5α-cholan-22-one, m. 190-1°, [α]D -62°, unchanged upon heating with dioxane and H2SO4, but gave oily products when heated with POCl3 and C5H5N or with Ac2O. IX (1 g.) and 2 g. KHSO4 heated 15 min. at 170-5°/about 25 mm., cooled, treated with Et2O, the Et2O phases from 3 runs worked up, and the crude product chromatographed on 150 g. Al2O3 gave 0.33 g. oily material, 1.15 g. Et 3β,16α- diacetoxybisnor-5α-chol-17(20)-enate (XV), m. 140-1° (Et2O-hexane), [α]D -73°, and 0.90 g. 3β-acetoxy- 16α-hydroxybisnor-5α-chol-17(20)-enic 22 → 16-lactone (XVI), m. 239-40° (Me2CO-hexane), [α]D -165°. A similar run with a longer reaction time gave more XVI at the expense of XV. IX (100 mg.) and 300 mg. CuSO4 heated 0.5 hr. at 180°/25 mm. and the product chromatographed yielded 82 mg. oil and 7 mg. XV. IX (100 mg.) in 5 cc. C5H5N heated 0.5 hr. on the water bath with 3 cc. POCl3 in 5 cc. C5H5N gave 80 mg. oil. IX (200 mg.) in 30 cc. Ac2O refluxed 2 hrs., evaporated, and the residue chromatographed on 5 g. Al2O3 gave 175 mg. oil. XV (100 mg.) and 200 mg. KHSO4 heated 0.5 hr. at 175°/25 mm. and the crude product chromatographed on 5 g. Al2O3 yielded 36 mg. XV and 24 mg. XVI, m. 236-9°. XV (120 mg.) and 450 mg. KOH in 15 cc. 95% MeOH refluxed 2 hrs., treated with H2O and Et2O, the aqueous alkaline solution acidified with dilute HCl, and the product isolated with Et2O yielded 24 mg. XVI, m. 236-9° (Me2CO-hexane). XI (250 mg.) and 500 mg. KHSO4 heated 0.5 hr. at 170-80°/20 mm. and the product chromatographed on 12 g. Al2O3 yielded 103 mg. lactone, C24H34O4 (XVII), needles, m. 165-6° (Et2O-hexane), [α]D -49°, and 78 mg. hydroxylactone, C24H36O5, m. 250-2° (Me2CO-hexane), [α]D -65°. XVII (80 mg.), 300 mg. KOH, and 10 cc. 90% MeOH refluxed 2 hrs., diluted with Et2O and H2O, the aqueous alkaline layer acidified with dilute HCl, and the product isolated with EtOAc gave 62 mg. lactone, m. 175-7°, which reacetylated yielded XVII. XV (2 g.) in 60 cc. glacial AcOH hydrogenated 4 hrs. at 24°/764 mm. gave 1.71 g. Et 3β,16α-diacetoxy-20-isobisnor-5α-cholanate (XVIII), m. 129-30° (hexane), [α]D -51°; 2nd polymorphic modification m. 159-60°. XVIII (1.5 g.) and 15 g. KOH in 150 cc. 85% EtOH refluxed 8 hrs., treated with H2O and Et2O, the aqueous layer

washed with Et2O, acidified with dilute HCl, and the product isolated with EtOAc gave 1.13 g. 3β,16α-dihydroxy-20-isobisnor-5α-cholanic acid (XIX), which in 100 cc. absolute MeOH treated 16 hrs. at 0° with excess CH2N2-Et2O gave 0.97 g. Me ester (XX), m. 181-2° (Me2CO-hexane), [α]D -7°; diacetate of XX m. 169-70°, [α]D -50°. XVIII (200 mg.), 750 mg. KOH, and 25 cc. 95% MeOH refluxed 2 hrs. gave 76 mg. XX; the aqueous alkaline layer from the processing procedure acidified and extracted with EtOAc gave 68 mg. XIX, m. 180-2°. XVIII (0.5 g.) in 125 cc. tetrahydrofuran reduced with 1.25 g. LiAlH4 in 60 cc. Et2O gave 0.32 g. 20-isobisnor-5α-cholane-3β,16α,22-triol (XXI), m. 269-70° (MeOH), [α]D -23° (C5H5N); triacetate m. 151-2° (Et2O-hexane), [α]D -57°. XX (50 mg.) in 10 cc. tetrahydrofuran with 125 mg. LiAlH4 in 10 cc. Et2O yielded 35 mg. XXI. XX (1.1 g.) in 100 cc. glacial AcOH treated at 10° during 10 min. with 1 g. CrO3 in 10 cc. 90% AcOH, kept 1 hr. at 10° and 1 hr. at room temperature, and worked up yielded 0.74 g. Me 3,16-dioxo-20-isobisnor-5α-cholanate (XXII), m. 143-5° (EtAc-hexane), [α]D -110°. XXI (300 mg.) in 25 cc. AcOH with 250 mg. CrO3 in 2.5 cc. 90% AcOH gave 175 mg. acidic material, which in 20 cc. CH2Cl2 treated with CH2N2-Et2O during 16 hrs. at 0° gave 140 mg. XXII. XXII (100 mg.) in 20 cc. MeOH treated 16 hrs. at room temperature with 500 mg. NaBH4 in 4 cc. MeOH, the mixture worked up, the product (90 mg.) treated 16 hrs. at room temperature with 4 cc. C5H5N and 2 cc. Ac2O, separated into 17 mg. acidic and 76 mg. neutral material, and the latter chromatographed on 5 g. Al2O3 yielded 48 mg. 3β-acetoxy-16β-hydroxy-20-isobisnor-5α-cholanic 22 → 16-lactone (20-isotigonein lactone acetate) (XXIII), m. 226-8° (hexane), [α]D -36°. Crude XIX (100 mg.), 1 cc. concentrated HCl, and 1 cc. H2O in 20 cc. glacial AcOH refluxed 2 hrs., poured into ice, the mixture extracted with EtOAc, the extract worked up, and chromatographed on 5 g. Al2O3 yielded 58 mg. XXIII, m. 224-6°, [α]D -35°. XXIII (60 mg.) and 750 mg. KOH in 25 cc. 90% MeOH refluxed 2 hrs., washed with EtOAc, acidified, the product isolated with EtOAc, and acetylated gave 56 mg. 20-normal isomer (tigogenin lactone acetate (XXIV) of XXIII, m. 219-21° (CH2Cl2-hexane), [α]D -49°. XXIII was also rearranged to XXIV with NaOMe in C6H6 at 78° in a sealed tube. XVI (500 mg.) in 20 cc. EtOAc hydrogenated 1.5 hrs. at 27°/754 mm. over 50 mg. prereduced PtO2 gave 445 mg. 3β-acetoxy-16α-hydroxy-17- isobisnor-5α-cholanic 22 → 16-lactone (XXV), m. 199-201° (CH2Cl2-hexane), [α]D 21°. XXV (200 mg.) in 50 cc. tetrahydrofuran and 500 mg. LiAlH4 in 20 cc. Et2O gave 145 mg. 17-isobisnor-5α-cholane-3β,16α,22-triol (XXVI), m. 245-7° (MeOH), [α]D -45° (C5H5N); triacetate m. 100-1° (Et2O-hexane), [α]D -45°. XXVI (200 mg.) in 25 cc. AcOH oxidized with 200 mg. CrO3 in 2 cc. 90% AcOH, worked up in the usual manner, the acidic fraction (140 mg.) in 20 cc. CH2Cl2 treated 16 hrs. at 0° with CH2N2-Et2O, and the product chromatographed on 10 g. Al2O3 yielded 115 mg. Me 3,16-dioxo-17-isobisnor-5α- cholanate (XXVII), m. 131-3° (CH2Cl2-hexane), [α]D -67°. XXV (200 mg.) in 50 cc. 90% MeOH refluxed 2 hrs. and worked up with H2O and Et2O gave 175 mg. 3β-acetoxy-16α-hydroxy-17-iso- 20-isobisnor-5α-cholanic 22 → 16-lactone (XXVIII), m. 190-1° (Me2CO-hexane), [α]D 13°. XVIII (200 mg.) in 50 cc. tetrahydrofuran and 500 mg. LiAlH4 in 20 cc. Et2O yielded 135 mg. 17-iso-20-isobisnor-5α-cholane-3β,16α,22-triol (XXIX), m. 189-91° (MeOH-EtOAc), [α]D -19° (C5H5N); triacetate m. 109-10° (Et2O-hexane), [α]D -71°. XXIX (100 mg.) in 10 cc. AcOH oxidized with 100 mg. CrO3 in 1 cc. 90% AcOH, worked up, and the acidic product (48 mg.) chromatographed on 2 g. Al2O3 yielded 38 mg. Me 3,16-dioxo-17-iso-20-isobisnor-5α- cholanate (XXX), m. 121-3°, [α]D -121°. Natural XXIV reduced with LiAlH4 gave about 80% bisnor-5α-cholane-3β,16β,22-triol (XXXI), m. 246-9°, [α]D 15° (C5H5N); triacetate m. 117-18° (Et2O-hexane), [α]D 52°. XXII (700 mg.) and 9 g. KOH in 300 cc. 93% aqueous MeOH refluxed 2 hrs., worked up in the usual manner, and the acidic material (620 mg.) in 100 cc. CH2Cl2 treated 16 hrs. at 0° with CH2N2-Et2O yielded 640 mg. Me 3,16-dioxobisnor-5α-cholanate (XXXII), m. 219-22° (EtCOMe),

[α]D -108°. XXVII (100 mg.) treated with base and reacetylated yielded 88 mg. XXXII, m. 214-19°. XXX (20 mg.) gave similarly 14 mg. XXXII, m. 218-20°. XXXI oxidized with CrO3 in AcOH and the acidic product esterified with CH2N2-Et2O gave about 40% XXXII, m. 220-2°, [α]D -108°. XXXII (1 g.), 1.5 g. p-MeC6H4SO3H.H2O, 12 cc. (CH2OH)2, and 1.5 l. C6H6 refluxed 5 hrs. with the removal of 200 cc. C6H6, treated again with 1.5 g. p-Me2CH4SO3H, refluxed 6 hrs. with the removal of 300 cc. C6H6, treated 10 min. with 3 g. NaOH in 50 cc. 95% MeOH, worked up, and the crude product chromatographed on 60 g. Al2O3 yielded 0.72 g. Me 3,3:16,16-bis(ethylenedioxy)bisnor-5α-cholanate (XXXIII), m. 196-8° (Me2CO-hexane), [α]D -24°. XXXIII (1.13 g.) in 300 cc. tetrahydrofuran treated dropwise during 15 min. with 1.5 g. LiAlH4 in 75 cc. Et2O under N, the mixture stirred 1 hr., kept 16 hrs., and worked up gave 0.76 g. 3,3: 16,16-bis(ethylenedioxy)bisnor- 5α-cholan-22-ol (XXXIV), m. 235-7° (Me2CO), [α]D -18°. XXXIV (40 mg.) in 10 cc. 90% AcOH heated 1 hr. at 90°, diluted with H2O, the product dissolved in 10 cc. Et2O, and reduced with 50 mg. LiAlH4 in 2 cc. Et2O gave 26 mg. XXXI, m. 247-50° (MeOH), [α]D 14° (C5H5N). XXXIV (500 mg.) in 15 cc. C5H5N added dropwise to 350 mg. CrO3 in 15 cc. dry C5H5N, the mixture kept 4 hrs. at 37°, worked up, the crude product isolated with EtOAc, and chromatographed on 30 g. Al2O3 yielded 415 mg. 3,3:16,16-bis(ethylenedioxy)bisnor-5α-cholan-22-al(XXXV), m. 183-4° (Et2O-pentane), [α]D -21°. XXXV (50 mg.) in 10 cc. tetrahydrofuran reduced with 50 mg. LiAlH4 in 2 cc. Et2O at room temperature gave 41 mg. XXXIV, m. 235-7°. XXXV (80 mg.) in 7.5 cc. C6H6 added dropwise with stirring to iso-AmMgBr from 18 mg. Mg and 122 mg. iso-AmBr in 7.5 cc. Et2O under N, the mixture refluxed 4 hrs., and worked up gave 67 mg. 3,3:16,16-bis(ethylenedioxy)cholestan-22-ol (XXXVI), m. 195-6° (Me2CO-hexane), [α]D -20°. XXXVI (40 mg.) in 2 cc. C5H5N treated with 40 mg. CrO3 in 2 cc. C5H5N, the mixture kept 48 hrs. at 37°, worked up, and the product chromatographed on Al2O3 yielded 27 mg. 22-one analog (XXXVII) of XXXVI, m 134-5° (Et2O-pentane), [α]D -16°. XXXVII (20 mg.) in 5 cc. 80% AcOH heated 1 hr. at 90°, the product isolated with Et2O, and chromatographed on 3 g. Al2O3 gave 11 mg. cholestane-3,16,22-trione (XXXVIII), plates, m. 176-7°. XXXVIII (5 mg.) refluxed 1 hr. with 2 cc. 5% KOH-MeOH under N and the product isolated with Et2O yielded XXXIX, oil. EtOCH:CHCO2Et (108 g.) and 115 g. MeCH:CHCH2OH containing 1 g. Na heated to 220° until the gas evolution ceased, the residue dissolved in 500 cc. MeOH, refluxed 2 hrs. with 50 g. NaOH in 100 cc. H2O, diluted with H2O, and worked up with Et2O gave 25.8 g. CH2:CHCHMeCH2CO2H (XL), b25 78-80°, n20D 1.4366. XL (20 g.) in 200 cc. Et2O treated dropwise with stirring with 8 g. LiAlH4 in 400 cc. Et2O, the mixture stirred 2 hrs., and worked up gave 13.8 g. CH2:CHCHMeCH2CH2OH (XLI), b25 63-4°, n20D 1.4369. XLI (12 g.) and 2.25 cc. C5H5 treated dropwise during 0.5 hr. with 4.5 cc. PBr3, the mixture stirred 0.5 hr., and worked up gave 8.2 g. CH2:CHCHMeCH2CH2Br (XLII), b764 138-40°, n20D 1.4680. XXXV (300 mg.) in 10 cc. C6H6 added dropwise at room temperature with stirring to the Grignard reagent from 68 mg. Mg and 650 mg. XLII in 10 cc. Et2O under N, the mixture refluxed 2 hrs., worked up, and the product chromatographed on 18 g. Al2O3 yielded 265 mg. mixed C-25 isomeric 3,3: 16,16-bis(ethylenedioxy)-26-methylenecholestan-22-ol (XLIII), m. 143-57°, [α]D -18°. CrO3 (400 mg.) added slowly with cooling to 20 cc. C5H5N, the mixture kept 48 hrs. at 37° with 400 mg. XLIII, decomposed with MeOH, and the product isolated with EtOAc gave 340 mg. 22-one analog (XLIV) of XLIII, m. 145-8° (Et2O), [α]D -16°. XLIV (30 mg.) in 15 cc. 90% AcOH heated 1 hr. at 90°, the product isolated with Et2O, and chromatographed on 4 g. Al2O3 gave 18 mg. 26-methylenecholestane-3,16,22-trione, m. 161-5° (Et2O-pentane). XLIV (300 mg.) in 30 cc. EtOAc containing 3 drops of C5H5N ozonized at -18°, treated with 6 g. Raney Ni, refluxed 10 min., filtered, evaporated, the residue heated 0.5 hrs. at 90° with 30 cc. 80% AcOH, and worked up gave 195 mg. crude noncryst. aldehydes; the crude product dissolved in 90 cc. dry tetrahydrofuran, the solution reduced with 300 mg. NaBH4 in 90 cc. absolute iso-PrOH during 72 hrs. at room temperature, the

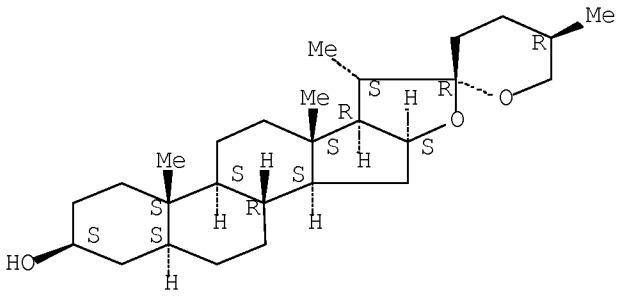
product isolated with EtOAc, heated 5 min. on the water bath with 30 cc. MeOH and 0.3 cc. 10% aqueous HCl, and chromatographed on 9 g. Al2O3 yielded 63 mg. mixture of II and III, needles, m. 178-82° (sublimed at 160°/0.01 mm.), [α]D -71°. II-III mixture (15 mg.) in 25 cc. EtOH and 6 cc. concentrated HCl refluxed 48 hrs. under N, diluted with 3 cc. concentrated HCl, refluxed 72 hrs., the product isolated with EtOAc, and chromatographed on Al2O3 gave 9 mg. II, m. 202-4° (Me2CO-hexane), [α]D -68°. II-III mixture (45 mg.) acetylated and the mixed acetates recrystd. from a relatively dilute EtOH solution gave 10 mg. acetate of III, octahedra, m. 175-8°, which refluxed 1 hr. with 20 cc. 3% KOH in 90% MeOH and worked up yielded 7 mg. III, m. 201-3° (Me2CO-hexane), [α]D -76°. 5α,25D-spirostan-3-one (XLV) (1 g.) in 150 cc. glacial AcOH treated with 1 cc. HBr-AcOH and then during 3 min. with stirring at room temperature with 1.3 g. Br in 20 cc. AcOH, the mixture kept 10 min., and worked up gave 0.88 g. 2α,4α,23-tribromo- 5α,25D-spirostan-3-one (XLVI), m. 196-8° (decomposition) (CH2Cl2-EtOAc).
Br (200 mg.) added to 15 cc. Me2CO, the mixture treated with 1 g. Na2CO3, shaken 20 min., filtered, added to 5 g. NaI in 100 cc. Me2CO, refluxed 0.5 hr., treated with 850 mg. XLVI, refluxed 12 hrs., worked up, the product refluxed 3 hrs. with 10 g. Zn dust in 100 cc. AcOH, worked up, and chromatographed on 40 g. Al2O3 yielded 280 mg. XLV and 165 mg. 25D-spirost-4-en-3-one (XLVII), m. 185-7° (CHCl3-Et2O), [α]D -7°. XLVII (150 mg.) in 50 cc. CH2:CMeCO2Ac refluxed 3 hrs. and worked up gave 115 mg. 25D-spirosta-3,5-dien-3-ol acetate (XLVIII), m. 181-2° (Et2O-MeOH), [α]D -113°. XLVIII (100 mg.) in 200 cc. EtOH added dropwise during 2 hrs. with stirring to 1 g. NaBH4 in 50 cc. 70% EtOH at 5°, the mixture kept 1 hr. at 5°, worked up, the product isolated with EtOAc, refluxed 1 hr. in 50 cc. EtOH with 3 drops concentrated HCl, again isolated with EtOAc, and chromatographed on 6 g. Al2O3 yielded 66 mg. diosgenin, m. 205-7°, (MeOH) [α]D -119°. 5α,25D-Spirost-9(11)-en-3β-ol acetate (XLIX) (75 mg.), m. 197-8°, in 15 cc. AcOH treated 48 hrs. at 37° with 75 mg. CrO3 in 5 cc. 85% AcOH, worked up, and the product chromatographed on 6 g. Al2O3 yielded 22 mg. XLIX and 18 mg. 3α-acetoxy-5α,25D-spirost-9(11)-en-12-one (L), m. 217-19° (MeOH), [α]D -9°. L (50 mg.) in 20 cc. dry Et2O added dropwise during 5 min. with stirring to 100 mg. Li in about 30 cc. liquid NH3, the mixture stirred 5 min., worked up, the product refluxed 2 hrs. with 20 cc. 3% KOH-MeOH (containing 2 cc. H2O), isolated with EtOAc, and chromatographed on 5 g. Al2O3 yielded 31 mg. hecogenin, m. 263-5° (Me2CO), [α]D 6°.

IT 77-60-1P, Tigogenin 470-01-9P, Neotigogenin 4948-43-0P, Neotigogenin, acetate 6870-79-7P, 25D-Spirost-4-en-3-one 6877-75-4P, 25D-Spirosta-3,5-dien-3-ol, acetate 121250-54-2P, 5α,25D-Spirost-9(11)-en-12-one, 3α-hydroxy-, acetate
RL: PREP (Preparation)
(preparation of)

RN 77-60-1 HCAPLUS

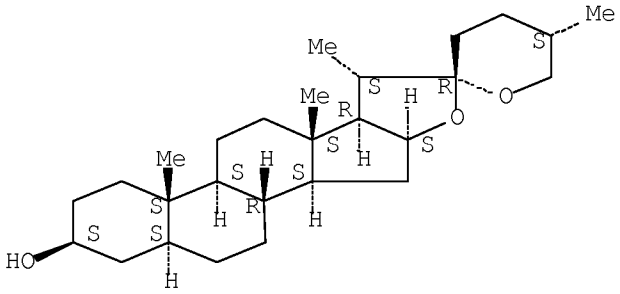
CN Spirostan-3-ol, (3β,5α,25R)- (CA INDEX NAME)

Absolute stereochemistry.



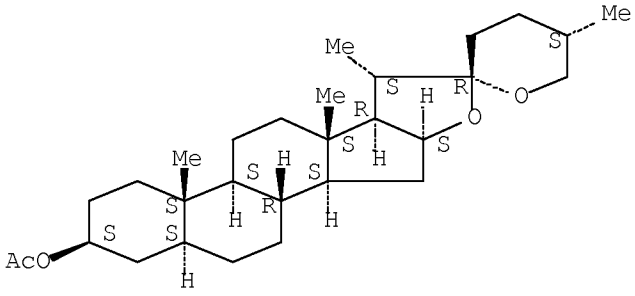
RN 470-01-9 HCAPLUS
CN Spirostan-3-ol, (3β,5α,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



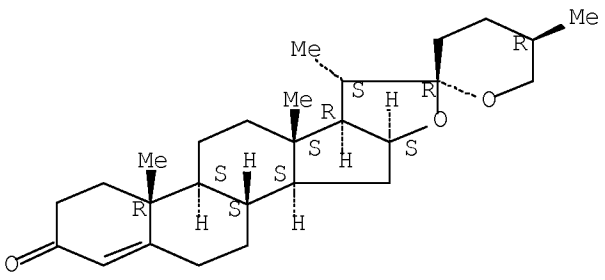
RN 4948-43-0 HCAPLUS
CN Spirostan-3-ol, acetate, (3β,5α,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



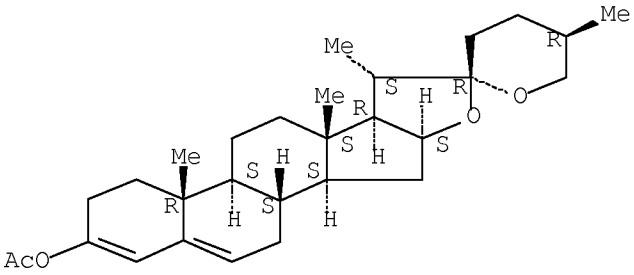
RN 6870-79-7 HCAPLUS
CN Spirost-4-en-3-one, (25R)- (CA INDEX NAME)

Absolute stereochemistry.



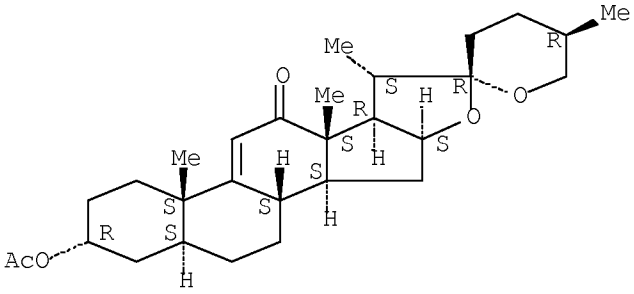
RN 6877-75-4 HCAPLUS
CN Spirosta-3,5-dien-3-ol, acetate, (25R)- (8CI) (CA INDEX NAME)

Absolute stereochemistry.



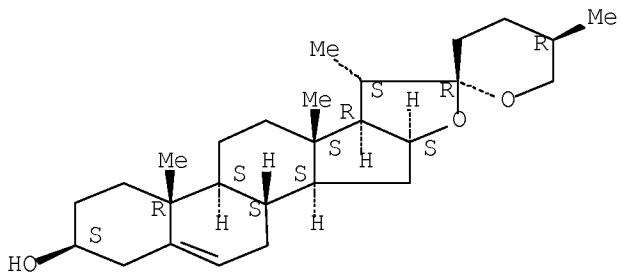
RN 121250-54-2 HCAPLUS
CN 5α,25D-Spirost-9(11)-en-12-one, 3α-hydroxy-, acetate (6CI)
(CA INDEX NAME)

Absolute stereochemistry.



IT 512-04-9P, Diosgenin
RL: PREP (Preparation)
(synthesis of)
RN 512-04-9 HCAPLUS
CN Spirost-5-en-3-ol, (3β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



L97 ANSWER 7 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1960:103641 HCAPLUS Full-text
DN 54:103641
OREF 54:19759e-i,19760a-i,19761a-i,19762a-b
TI Long-range effects in alicyclic systems. III. Relative rates of condensation of some steroid and triterpenoid ketones with benzaldehyde
AU Barton, D. H. R.; McCapra, F.; May, P. J.; Thudium, F.
CS Univ. Glasgow, UK
SO Journal of the Chemical Society (1960) 1297-1311
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable
AB cf. C.4 51, 13817b. The rates of alkali catalyzed condensation of a series of steroidal 3-ones with BzH (I) to give the corresponding 2-benzylidene derivs. were determined As in the earlier work with triterpenoid ketones, long-range effects produced by unsatd. substituents (especially the ethylenic linkage) and by other groups could be easily detected. There existed a quant. relation between the rates for structurally analogous steroidal and triterpenoid ketones such that rates could be expressed in terms of the rate of a saturated reference ketone multiplied by a series of group rate factors (f) each of which was characteristic of the nature and position of the substituent group. The possible role of polar factors in influencing rates of condensation of carbonyl substituted ketones was admitted, but the major importance of the new effects of conformational transmission was considered to have been again demonstrated for ketones having remotely placed ethylenic substitution. A cursory investigation of derivs. of β-decalone was shown, that, wherever structurally appropriate, the same effects could be recognized and were of the same quant. magnitude as in corresponding steroid and triterpenoid ketones. A preliminary account of this work was given earlier (CA 53, 17875b). Lanostane-3,11-dione (1.16 g.), 0.22 ml. (CH2OH)2, 10 mg. p-MeC6H4SO3H,and 50 ml. C6H6 refluxed 18 hrs., the solution poured into saturated aqueous Na3CO3, and the C6H6 layer separated gave 1.13 g. lanostane-3,11-dione 3-(ethylene ketal) (II), m. 140-1° (C6H6-MeOH), [α]D 31° (c 1.37, all rotations refer to CHCl3 unless otherwise specified). II (150 mg.) in 10 ml. refluxing PrOH treated during 1 hr. with 1 g. Na, 7 ml. PrOH added, the solvent removed, and the residue worked up as usual gave 131 mg. 11α-hydroxylanostan-3-one ethylene ketal (III), prisms, m. 165-6° (MeOH), [α]D 0° (c 1.88). Hydrolysis of 180 mg. III in 12 ml. AcOH and 3.5 ml. H2O 10 min. on the steam bath gave 150 mg. 11α-hydroxylanostan-3-one, prisms, m. 151-2° (aqueous MeOH), [α]D -6° (c 1.66). II (200 mg.) in 50 ml. dry Et2O refluxed 16 hrs. with 220 mg. LiAlH4, the excess reducing agent destroyed with EtOAc, and the mixture worked up as usual gave 165 mg. 11β-hydroxylanostan-3-one ethylene ketal (IV), m. 143-4° (MeOH), [α]D 30° (C 2.00). IV (270 mg.) in 35 ml. AcOH and 5 ml. H2O heated 10 min. gave 157 mg. 11β- hydroxylanostan-3-one, plates, m. 188-9° (ligroine), [α]D 28° (c 1.49). IV (279 mg.) treated 15 min. at room temperature with 12

drops aqueous 60% HClO4 in 15 ml. AcOH gave 211 mg. lanost-9 (11)-en-3-one, m. 113-14° (CHCl3-MeOH), [α]D 65° (c 2.67). 3β-Hydroxy-α-amyr-12-en-11-one (1.5 g.) in 100 ml. C6H6 added dropwise to 200 ml. Et2O containing MeMgI (from 8 ml. MeI), the Et2O distilled, the C6H6 solution refluxed 55 hrs., excess of saturated aqueous NH4Cl added, the C6H6 separated, the solvent evaporated, the residue left overnight at room temperature with 10 ml. C5H5N and 10 ml. Ac2O and chromatographed on Al2O3 gave 752 mg. 11-methylene-α-amyr-12-enyl acetate (V), m. 229 32° (CHCl3-MeOH), [α]D 143° (c 1.95), λ 246 mμ, ε 19,700. Hydrolysis of V gave the alc. and oxidation with C5H5N-CrO3 gave 11-methylene-α-amyr-12-en-3-one, m. 146-7° (aqueous MeOH), [α]D 208° (c 1.2), λ 247 mμ, ε 19,700. β-Amyrane-3,12-dione (1.7 g.) in 160 ml. (CH2OH)2 containing 60 mg. p-MeC6H4SO3H slowly distilled at 1.5 mm. during 2 hrs. and dilute aqueous KOH added gave 1.59 g. β-amyrane-3,12-dione 3-(ethylene ketal) (VI), m. 279-81° (C6H6-MeOH), [α]D -45° (c 1.64). VI (150 mg.) in 10 ml. refluxing PrOH treated during 1 hr. with 1 g. Na gave 121 mg. 12β-hydroxy-β-amyran-3-one ethylene ketal (VII), plates, m. 272-4° (C6H6-MeOH). Treatment of VII (167 mg.) with 5 ml. 90% AcOH 5 min. at 100° gave 87 mg. 12β-hydroxy-β-amyran-3-one, m. 210-13° (aqueous MeOH), [α]D 39° (c 1.54). VII (474 mg.) reduced with 900 mg. LiAlH4 in 150 ml. refluxing Et2O gave on chromatography 254 mg. 12α-hydroxy-β-amyran-3-one ethylene ketal (VIII), m. 261-3° (C6H6-MeOH), [α]D 16° (c 2.13). Elution with C6H6 gave 123 mg. VII. VIII treated with aqueous AcOH gave 12α-hydroxy-β-amyran-3-one, m. 252-5° (CHCl3-MeOH), [α]D 81° (c 1.11). Wolff-Kishner reduction of 1.9 g. 12-oxo-βamyranyl acetate gave after reacetylation 1.24 g. β-amyranyl acetate. Alkaline hydrolysis and oxidation with C5H5N-CrO3 gave β-amyran-3-one, m. 200-1° (CHCl3-MeOH), [α]D 41° (c 0.97). 7-Oxocholestanyl acetate was converted into 80% 7-methylenecholestanyl acetate, leaflets, m. 72-3° (alc.), [α]D -43° (c 0.95), ν 890 and 1650 cm.-1 Refluxing 0.5 hr. with MeOH-KOH gave 7-methylenecholestanol (IX), m. 115° (ligroine), [α]D -31° (c 1.14). IX (560 mg.) in 60 ml. Me2CO treated with a standard solution of CrO3 in concentrated H2SO4 under N with shaking 3 min., gave after extraction 530 mg. 7-methylenecholestanone, plates, m. 104-6° (aqueous alc.), [α]D -11° (c 0.94), v 1700, 890, and 1650 cm.-1 Hecogenin acetate (1.5 g.) in 20 ml. C6H6 treated 1 hr. at room temperature with MeMgI in Et2O, and warmed 45 min. at 40° gave 910 mg. 12β-hydroxy-12α-methyltigogenin (X), m. 197-9° (Et2O), [α]D -37° (c 1.00). X (720 mg.) in 70 ml. Me2CO treated 7 min. at 0° with standard oxidation mixture gave 600 mg. 12β-hydroxy-12α-methyltigogenone (XI), plates, m. 228-43°, prisms, m. 241-3° (aqueous alc.), [α]D -21° (c 1.06). XI (245 mg.) in 12 ml. C5H5N treated 16 hrs. at room temperature with POCl3 and then 2.5 hrs. at 55° and the product chromatographed on Al2O3 gave 12-methylenetigogenone (XII), m. 219-21° (ligroine), [α]D, -5° (c 0.88), ν 890 and 1650 cm.-1 XII (49 g.) in 50 ml. CH2Cl2 ozonized 1 hr. at -80° gave 12 mg. hecogenone. 11-Dehydrotigogenin oxidized with CrO3 to 11-dehydrotigogenone, irregular plates, m. 169-74° (MeOH), [α]D -20° (c 1.13). 9 (11)-Dehydrotigogenin oxidized to 9 (11)-dehydrotigogenone, m. 195-6.5° (MeOH), [α]D -45° (c 0.98). Ergosta-7,14,22-trienol (250 mg.) in 38 ml. C6H6, 10 ml. Me2CO, and 2 g. (iso-PrO)3Al refluxed 8 hrs. gave 70 mg. ergosta-7,14,22-trien-3- one (XIII), m. 150-2° (MeOH), [α]D -220° (c 0.96), λ 242 mμ, ε 9800. XIII was also prepared by CrO3-Me2COH2SO4 oxidation of ergosterol B3, but the yield was only 20%. Ergost-22-ene-3,11-dione (720 mg.) in 200 ml. (CH2OH)2 containing 60 mg. p-MeC6H4SO3H slowly distilled during 5 hrs. at 63°/1.5 mm., and the product treated with alc. KOH gave 640 mg. ergost-22-ene-3,11-dione 3-(ethylene ketal) (XIV), plates, m. 153-4° (MeOH), [α]D 19° (c 2.02). XIV (200 mg.) in 15 ml. refluxing PrOH treated with 1.5 g. Na gave 180 mg. 11α-hydroxyergost-22-en-3-one ethylene ketal (XV), needles, m. 184-5° (MeOH), [α]D -23° (c 1.5). XV (150 mg.)

hydrolyzed 10 min. with 80% aqueous AcOH gave 100 mg. 11α-hydroxyergost-22-en-3-one, m. 142-4° (ligroine), [α]D -19° (c 1.59). XIV (150 mg.) reduced with excess LiAlH4 in Et2O gave 120 mg. 11B-hydroxyergost-22-en-3-one ethylene ketal (XVI), m. 155-6° (aqueous MeOH), [α]D 0° (c 1.6). Hydrolysis of XVI with aqueous AcOH gave 60 mg. 11β-hydroxyergost- 22-en-3-one, m. 170-2° (ligroine), [α]D 12° (c 2.0). 3β-Acetoxyergostane-7,11-dione hydrolyzed as usual gave 3β-hydroxyergostane-7,11-dione (XVII), m. 177-9° (MeOH), [α]D -6° (c 2.73). Oxidation of XVII with CrO3AcOH and C6H6 gave ergostane-3,7,11-trione, m. 186-8°, [α]D 16.7° (c 1.92). Similar oxidation of 3β-hydroxyergost-22-en-7,11-dione gave ergost-22-en-3,7,11-trione, plates, m. 194-5° (MeOH), [α]D (c 2.28). Ergosta-8,22-dienol oxidized with CrO3 in C5H5N to ergosta-8,22-dienone, plates, m. 168-70° (MeOH), [α]D 47° (c 0.30). 17β-Hydroxyandrostan-3-one hexahydrobenzoate (0.8 g.) in 10 ml. C6H6 and 10 ml. MeOH treated with 5 mg. p-MeC6H4SO3H gave 0.5 g. 3,3-dimethoxyandrostan-17β-yl hexahydrobenzoate (XVIII), m. 130-2°, [α]D 12° (c 2.03). XVIII reduced with LiAlH4 gave 0.3 g. 3,3-dimethoxyandrostan-17β-ol, m. 180-2° (aqueous MeOH), [α]D 14° (c 1.68). The ketal (0.3 g.) in 10 ml. MeOH and 2 ml. 4N H2SO4 left 1 hr. at room temperature, poured into H2O, extracted with Et2O, and processed as usual gave 0.2 g. 17β-hydroxyandrostan-3-one, m. 178-9° (aqueous MeOH), [α]D 32° (c 1.91). This procedure gave a better yield than hydrolysis of the hexahydrobenzoate in the presence of the 3-one. 3β-Hydroxy-11 -oxobisnorallocholanic acid (0.8 g.) in 50 ml. C6H6, oxidized with a slight excess of CrO3 in aqueous AcOH gave 0.6 g. 3,11-dioxobisnorallocholanic acid, plates, m. 258-61° (alc.), [α]D 52° (c 2.54). Stigmastanone (0.5 g.) in 50 ml. 0.1N alc. KOH treated 24 hrs. at room temperature in the dark with 0.5 g. I gave 310 mg. 2-benzylidenestigmastanone (XIX), m. 151-2° (MeOH-C6H6), [α]D -108° (c 1.46), λ 294 mμ, ε 16,200. Addition of H2O to the mother liquor and extraction with Et2O gave 80 mg. more material. XIX (563 mg.) in 100 ml. CHCl3 at -60° ozonized during 20 min., 5 ml. H2O added, the CHCl3 evaporated, and the oil dissolved in 2% aqueous KOH, washed, and acidified gave 50% 2,3-secostigmastane-2,3-dioic acid, plates, m. 230-2° (C6H6), [α]D 33° (c 0.98). Ergost-22-ene-3,11-dione (0.3 g.) in 25 ml. 0.1N alc.-KOH treated 24 hrs. with 300 mg. I at room temperature in the dark gave 190 mg. 2-benzylideneergost-22-ene-3,11-dione, plates, m. 191-2° (alc.), [α]D -7° (c 1.52), λ 294 mμ, ε 17,000. 3,11-Dioxobisnorallocholanic acid (0.2 g.) in 25 ml. 0.1N alc.-KOH treated as above with 0.3 g. I, poured into H2O, acidified, and extracted gave 150 mg. 2-benzylidene-3,11-dioxobisnorallocholanic acid, m. 268-70° (MeOH-C6H6), [α]D -24° (c 2.28), λ 294 mμ, ε 16,800. 7-Methylenecholestanone (100 mg.) similarly yielded 65 mg. 2-benzylidene-7-methylenecholestanone, m. 145-7° (MeOH-C6H6), [α]D -178° (c 1.16), λ 294 mμ, ε 17,700. Ergost-8(14)-enone similarly gave 2-benzylideneergost- 8(14)-en-3-one, m. 162-3° (C6H6-MeOH), [α]D -18° (c 2.4), λ 294 mμ, ε 17,000. 17-Hydroxyandrostan-3-one (65 mg.) with I as above gave 50 mg. 2-benzylidene-17-hydroxyandrostan-3-one, m. 190-1° (MeOH), [α]D -140° [c 1.8), λ 294 mμ, ε 16,600. 17β-Hydroxy-4,4-dimethylandrost-5-en-3-one (100 mg.) converted into 50 mg. 2-benzylidene-17β-hydroxy-4,4- dimethylandrost-5-en-3-one, prisms, m. 159-61° (MeOH-C6H6), [α]D -148° (c 1.45), λ 294 mμ, ε 16,500. 4,4-Dimethylergosterone (0.3 g.) in 50 ml. tetrahydrofuran and 100 ml. EtNH2 at 0° treated with Li, the solvent removed in vacuo, the residue oxidized at 0° with CrO3 in Me2CO, and the product chromatographed on Al2O3 gave 150 mg. product, m. 176-80°, [α]D -33° (c 1.36). Further elution gave 100 mg. 4,4-dimethylergosta-7,22-dien-3-one (XX), m. 143-5° (MeOH), [α]D -37° (c 1.36). XX (50 mg.) treated with I gave 25 mg. 2-benzylidene-4,4-dimethylergosta-7,22-dien-3-one (XXI), m. 133-5° (MeOH-C6H6), [α]D -111° (c 1.9), λ 289 mμ, ε 17,300. I condensed with ergosta-7,22-dien-3-one gave 800 mg. oil derivative, λ 294 mμ, ε 13,500. This taken up in 10 ml.

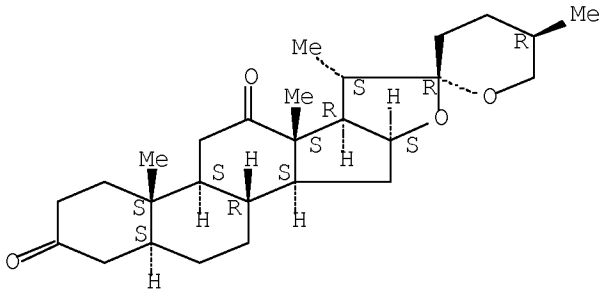
C6H6 refluxed 14 hrs. in a solution of 200 mg. K in 10 ml. tert-BuOH and 5 ml. MeI gave 250 mg. XXI. Cholestanone (100 mg.) in 20 ml. 0.1N MeOH-KOH treated at room temperature with 100 mg. I gave 80 mg. 2-(α-hydroxybenzyl)cholestanone, m. 188-90° (MeOH-C6H6), [α]D -71° (c 1.12). On treatment with alc. KOH under the conditions of a kinetic run this afforded in 5 min. I, 90% cholestanone, and 10% benzylidenecholestanone. Treatment of 50 mg. of the ketol with 20 ml. N alc. HCl gave the benzylidene derivative, amorphous, λ 294 mμ, ε 16,000. trans-β-Decalone (0.7 g.) in 25 ml. 0.1N alc. KOH treated 30 hrs. at room temperature in the dark with 2.6 g. I, and working as in earlier examples and trituration with ligroine gave 405 mg. 3-benzylidene-trans-β-decalone (XXII), prisms, m. 92-3° (ligroine), λ 292 mμ, ε 17,400. XXII (351 mg.) in 100 ml. CHCl3 was ozonized 0.5 hr. at -20° until the absorption at 292 mμ disappeared. The solution worked up as above gave 250 mg. trans-cyclohexylidene-1,2-diacetic acid, prisms, m. 164-5°. Benzylidene derivative of stigmastanone (21.2 mg.), 19.8 mg. benzylidene of ergost-8(14)-en-3-one, and 10.4 mg. XXII was treated with a 10 molar excess of I in 0.1N alc. KOH; in 20 hrs. there was no change in the intensity of the ultraviolet absorption and no increase in the 330 mμ region. 2α-Methylcholestanone (19.8 mg.) treated with I in alc. KOH as above gave 12 mg. unchanged material. The following ketones were treated under the conditions of a kinetic run: 3-hydroxycholestan-7-one, hecogenin, 3β-hydroxyergost-22-ene-7,11-dione, and 3β-hydroxyergost-22-en-11-one. In each case there was no appearance of ultraviolet absorption and the ketone was recovered unchanged.

IT 2137-20-4P, Hecogenone 7361-26-4P, Tigogenone, 9(11)-dehydro- 15401-31-7P, Tigogenin, 12β-hydroxy-12-methyl- 16127-92-7P, Tigogenone, 11-dehydro- 117917-08-5P, Tigogenone, 12β-hydroxy-12-methyl-
RL: PREP (Preparation)
(preparation of)

RN 2137-20-4 HCAPLUS

CN Spirostan-3,12-dione, (5α,25R)- (CA INDEX NAME)

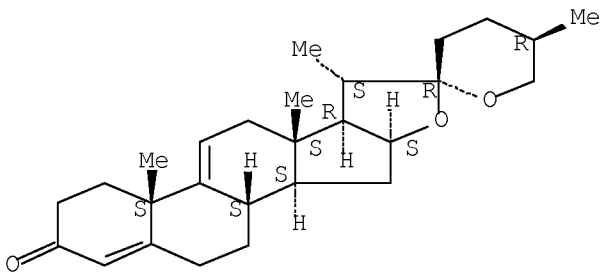
Absolute stereochemistry.



RN 7361-26-4 HCAPLUS

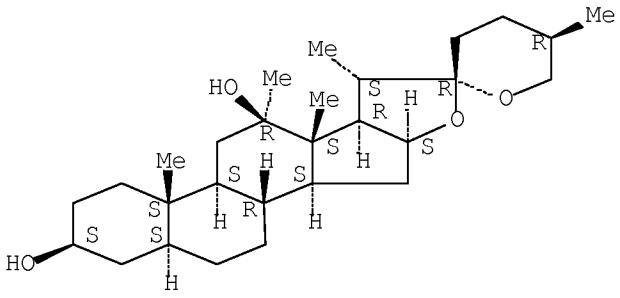
CN Spirosta-4,9(11)-dien-3-one, (25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



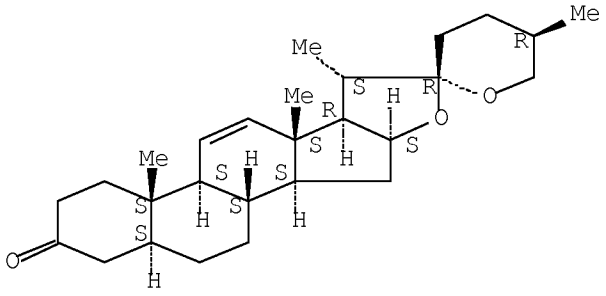
RN 15401-31-7 HCAPLUS
CN Spirostan-3,12-diol, 12-methyl-, (3β,5α,12β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



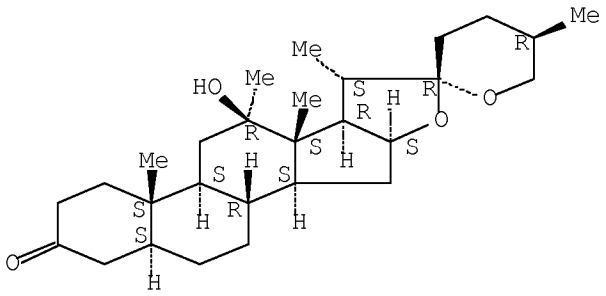
RN 16127-92-7 HCAPLUS
CN Spirost-11-en-3-one, (5α,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 117917-08-5 HCAPLUS
CN Tigogenone, 12β-hydroxy-12-methyl- (6CI) (CA INDEX NAME)

Absolute stereochemistry.



L97 ANSWER 8 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1960:28947 HCAPLUS Full-text
DN 54:28947
OREF 54:5738i,5739a-i,5740a-e
TI Steroidal components of domestic plants. XIX. Structure of kogagenin, a sapogenin from Dioscorea tokoro
AU Takeda, Kenichi; Kubota, Tokuo; Shimaoka, Ariyoshi
CS Shionogi & Co., Ltd., Osaka
SO Tetrahedron (1959), 7, 62-9
CODEN: TETRAB; ISSN: 0040-4020
DT Journal
LA Unavailable
AB cf. C.A. 53, 16206f. Kogagenin (I), a steroidal sapogenin isolated from the epigeous part of D. tokoro, was the 1st example of a naturally occurring spirostan tetrol. I, C27H44O6, [α]D -27° (C5H5N), m. 318-22° (decomposition), λ 10.90, 11.10 μ, (600 mg.) refluxed 2 hrs. in 6 ml. Ac2O and 3 ml. C5H5N and the product isolated with C6H6 gave I triacetate (II), m. 249-52°, [α]D -26° (c 1.0, CHCl3). I was a 25D-sapogenin and since II still showed an infrared absorption OH band, I was assumed to be a 25D-tetrahydroxyspirostan. I (500 mg.) refluxed 22 hrs. in 500 ml. Me2CO and 200 ml. C6H6 with 500 mg. p-MeC6H4SO3H and the neutralized (Na2CO3) solution concentrated in vacuo, extracted with C6H6 and the washed and dried extract evaporated, the crystalline residue chromatographed on 15 g. Al2O3, and eluted with 1:1 C6H6-CHCl3 and CHCl3 gave 316 mg. material, recrystd. (CHCl3-MeOH) to give 260 mg. I acetonide (III), m. 273-5°, [α]D -23° (c 1.15, CHCl3). Further elution with 1:1 CHCl3-MeOH gave 230 mg. I. II (500 mg.) in 5 ml. C5H5N at 0° treated dropwise with 0.50 g. SOCl2 in 2 ml. C5H5N and the mixture kept 1 hr. at 0°, diluted with ice H2O and extracted with Et2O, and the washed (dilute HCl, aqueous NaHCO3, H2O) and dried extract evaporated yielded 490 mg. oil, crystallized (MeOH) to give 395 mg. anhydrokogagenin triacetate (IV), m. 171-3°, [α]D 33° (c 1.0, CHCl3). IV (500 mg.) refluxed 1 hr. in 20 ml. 1.5% KOH-MeOH and the cooled mixture diluted with H2O, filtered, and the precipitate recrystd. (MeOH) gave anhydrokogagenin (V), m. 240-3°, [α]D -70° (c 1.0, CHCl3), neg. Rosenheim test. II was not affected by CrO3C5H5N oxidation and the ready dehydration to IV showed I to have a cis-αglycol group and a tertiary OH function. IV (100 mg.) in 7 ml. AcOH hydrogenated 30 min. with 100 mg. prereduced PtO2 and the filtered solution evaporated gave 45 mg. authentic tokorogenin triacetate (VI), m. 253-5°, [α]D -20° (c 1.0, CHCl3), saponified with 3% KOH-MeOH to tokorogenin, m. 266-8° (MeOH). The mother liquors from VI concentrated and the residue chromatographed on 3 g. Al2O3, the column washed free from 5 mg. VI with 1:1 petr. ether-C6H6, and eluted with C6H6 and 19:1 C6H6Et2O gave 35 mg. dihydrotokorogenin triacetate (VII), m. 167-9°, [α]D 40° (c 1.0, CHCl3), λ 2.83 μ, but no spiroketal bands at 10.19, 10.90, 11.10, 11.58 μ, identical with a specimen prepared by catalytic

reduction of authentic VI. Accordingly, I was established as a hydroxytokorogenin. IV (300 mg.) in 5 ml. C5H5N and 350 mg. OsO4 in 10 ml. C6H6 kept 53 hrs. in the dark at room temperature and the mixture saturated with H2S, filtered, and the filtrate evaporated in vacuo yielded 150 mg. diol triacetate (VIII), m. 252-4°, [α]D -44° (c 1.0, CHCl3). VIII (100 mg.) in 10 ml. AcOH kept overnight at room temperature with 0.7 g. Pb(OAc)4 in 20 ml. AcOH and diluted with H2O, extracted with Et2O, and the washed and dried ext evaporated produced a gum, λ 5.85 μ (strong), giving a pos. triphenyltetrazolium test, showing the presence of a CHO group and limiting the position of the double bond in IV to Δ5 (or Δ4) or Δ14. IV (450 mg.) in 2 ml. C5-H5N and 2 ml. Ac2O refluxed 5.5 hrs. with 0.3 g. EtNH2.HCl and the cooled mixture poured onto ice, extracted with Et2O, the furostene taken up in 9 ml. AcOH and treated dropwise with 0.3 g. CrO3 in 3 ml. 80% AcOH, the mixture stirred 2 hrs. at room temperature and diluted with H2O, extracted with Et2O and the washed and dried extract evaporated, the gummy solid saponified with 1% alc. KOH and the product reacetylated, purified by chromatography, and recrystd. (dilute alc.) yielded 95 mg. 5, 16-pregnadiene-1β,2β,3α-triol-20-one triacetate (IX), m. 150-2°, [α]D 168° (c 1.0, CHCl3), λ 239 mμ (log ε 4.00, alc.), establishing the presence of a Δ16-20-ketone group without addnl. conjugation. V (100 mg.) refluxed 6 hrs. in 30 ml. Me2CO containing 10 mg. p-MeC6H4SO3H and the neutralized (NaHCO3) solution concentrated in vacuo, extracted with Et2O, the product chromatographed, and eluted with 9:1 petr. ether-C6H6 and with 4:1-1:1 petr. ether-C6H6 gave the diene acetonide (X), m. 162-4° (MeOH), [α]D -115° (c 1.0, CHCl3), λ 236 mμ (log ε 4.31, alc.), and 93 mg. 25D-spirost-5-ene-1β,2β,3α-triol 1,2-acetonide (XI), m. 208-10°(MeOH), [α]D -61° (c 1.0, CHCl3). XI (80 mg.) in 4 ml. C5H5N containing 0.5 g. POCl3 heated 45 min. on a steam bath and the solution poured onto crushed ice, extracted with Et2O, and the oily product crystallized (MeOH) yielded 15 mg. X. Attempts to obtain a Δ4-3-oxo derivative of I by oxidation of XI with CrO3C5H5N complex, with CrO3-Me2CO-H2SO4, or by Oppenauer oxidation were unsuccessful with almost quant. recovery of XI. III (120 mg.) in 3 ml. C5H5N added at 0° to the complex from 150 mg. CrO3 and 1.5 ml. C5H5N and the mixture kept 16 hrs. at room temperature, extracted with Et2O, and the product crystallized (MeOH) gave a crude ketone (XII), m. 189-91° (decomposition), λ 2.84, 5.76 μ, contaminated by 10% α,β-unsatd. ketone (XIII). XII (80 mg.) chromatographed in 1:1 petr. ether-C6H6 on SiO2 gel and eluted with 9:1 C6H6-CHCl3 yielded 54 mg. material, m. 193-8°, λ 246 mμ (log ε 4.10, alc.), recrystd. (MeOH) to give XIII, m. 197-200°, [α]D -100° (c 1.0, CHCl3), λ 246 mμ (log ε 4.15, alc.), λ 5.93, 6.16 μ, but no OH absorption. XII (20 mg.) in 5 ml. MeOH kept overnight with 0.5 ml. 10% aqueous KOH and diluted with H2O, neutralized with dilute HCl, and extracted with Et2O yielded 15 mg. 25D-spirosta-1,4-dien-2-ol-3-one (XIV), m. 224-7°, [α]D -102° (c 0.36, CHCl3), λ 2.96, 6.09, 6.17 μ (Nujol), λ 254 mμ (log ε 4.13, alc.), giving reddish purple color with alc. FeCl3. XIV refluxed with alc. o-(H2N)2C6H4 produced an orange-yellow quinoxa-line. I (98 mg.) in 4 ml. CHCl3 acetylated overnight at room temperature with 1 ml. Ac2O and 4 ml. C5H5N gave 87 mg. I diacetate (XV), m. 275-7°, [α]D -13° (c 1.1, CHCl3). XV (80 mg.) in 6 ml. alc. free CHCl3 concentrated to 5 ml. and diluted with 4 ml. C5H5N, the mixture treated dropwise at -15° with 12 ml. 10% COCl2-MePh and the mixture warmed at 15° 1 hr., kept overnight at 15-20° and the COCl2 decomposed with ice, the mixture diluted with H2O and Et2O and the washed and dried Et2O layer evaporated, the gum chromatographed on 2 g. Al2O3, and eluted with C6H6 gave 37 mg. 25D-spirostan-1β,2β,3α,5β-tetrol 1,5-carbonate 2,3-diacetate, m. 169-72°, [α]D 27° (c 1.1, CHCl3), λ 5.66, 5.72, 8.08, 8.19, 8.40 μ (CS2), no OH band. Further elution with 1:1 CHCl3MeOH yielded 15 mg. impure XV, m. 257-66°. The likelihood that I should have the same cis configuration of the A/B ring junction as yonogenin and tokorogenin was strengthened by the close

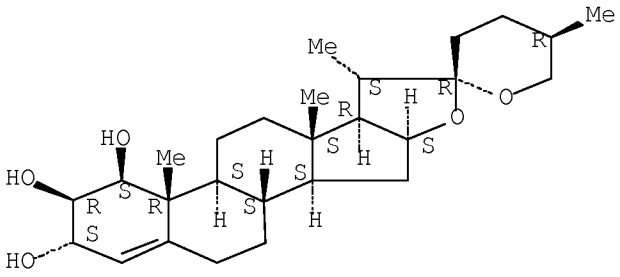
resemblance of the rotatory dispersion curves of XII and 25D,5β-spirostan-1β,2β-diol-3-one acetonide, derived from tokorogenin acetonide. From the formation of XV it was concluded that the OH group at C-5 in I was β-oriented and accordingly I was described as 25D-spirostan-1β,2β,3α,5β-tetrol.

IT 6869-44-9, 25D-Spirost-4-ene-1β,2β,3α-triol
133326-87-1, Kogagenin, anhydro-
(and derivs.)

RN 6869-44-9 HCAPLUS

CN Spirost-4-ene-1,2,3-triol, (1β,2β,3α,25R)- (9CI) (CA INDEX NAME)

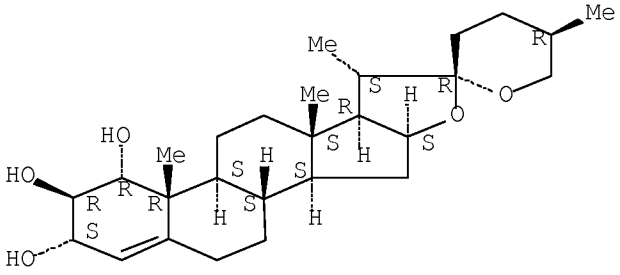
Absolute stereochemistry.



RN 133326-87-1 HCAPLUS

CN Kogagenin, anhydro- (6CI) (CA INDEX NAME)

Absolute stereochemistry.

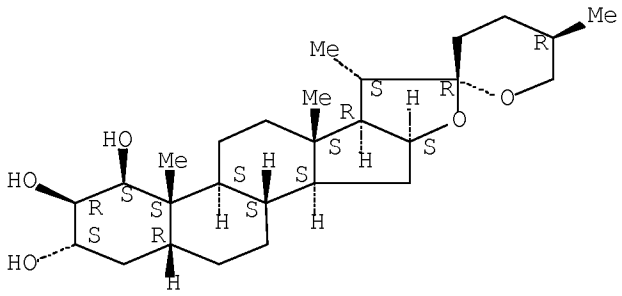


IT 547-01-3P, Tokorogenin 1255-15-8P, 25D-Spirosta-1,4-dien-3-one, 2-hydroxy-
RL: PREP (Preparation)
(preparation of)

RN 547-01-3 HCAPLUS

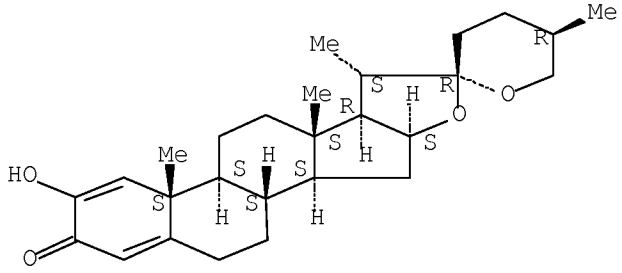
CN Spirostan-1,2,3-triol, (1β,2β,3α,5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 1255-15-8 HCAPLUS
CN Spirosta-1,4-dien-3-one, 2-hydroxy-, (25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L97 ANSWER 9 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1958:88167 HCAPLUS Full-text
DN 52:88167
OREF 52:15559f-i,15560a-b
TI The structure of tokorogenin
AU Morita, Katsura
CS Takeda Pharm. Inds., Ltd., Osaka
SO Pharmaceutical Bulletin (1957), 5, 494-6
CODEN: PHBUA9; ISSN: 0369-9471
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB The structure of the previously isolated (Nishikawa, et al., C.A. 49, 14785d) tokorogenin (I) is here established. Oxidation of I by CrO_3 in AcOH gave tokorogenic acid (II), m. 250°; $[\alpha]_D^{23}$ -26.3°; anhydride (with Ac_2O) (III), m. 268° (ν (Nujol) 1800, 1755 $cm.^{-1}$); di-Me ester (with CH_2N_2) (IV), m. 157°. II with MeOH-HCl gave the α-mono-Me ester (V), m. 185°, also formed from III with MeONa; whereas IV hydrolyzed by NaOH gave the β-mono- Me ester, m. 208°. I gave its acetonide (VI), m. 303°, hydrolyzed back to I by hot AcOH. VI with p-$MeC_6H_4SO_2Cl$ in C_5H_5N gave its tosyl ester, m. 203° (decomposition), which was hydrolyzed by hot AcOH to the 3-tosyl ester of I, and this in turn gave with MeOH-KOH the epoxide (VII), m. 235°. VII (oxidized by CrO_3 in C_5H_5N gave the α,β-epoxyketone (VIII), m. 236°, which treated with $CrCl_2$ gave the α,β-unsatd. ketone, m. 219° (λ 225 mμ at ε 7690), catalytically hydrogenated (Pd-C) to the saturated ketone, m. 182°, and this was finally reduced by the Huang-Minlon reaction to the known 5β-25D-spirostan (IX), m. 137°. Thus the 1-and 2-HO groups in I are shown to be cis, and the 3-HO group trans.

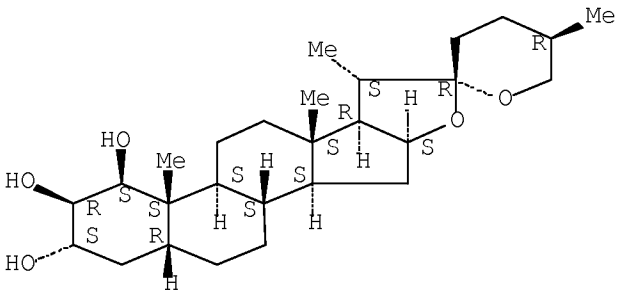
Reduction of VII by LiAlH4 gave 1β,3β-dihydroxysapogenin, m. 238°, which formed neither an acetonide nor an epoxy compound A 2nd series of reactions led also to IX from VI. Oxidation of VI by CrO3 in C5H5N gave the 3-oxo derivative (HO changed to :0) (X), m. 229°, which was hydrolyzed by hot AcOH to the dihydroxyketone (XI), m. 225°. With alkali, both X and XI gave the enol form of the α-diketone (XII), m. 225°, (λ 269 mμ at ε 6900), oxidized by alkaline H2O2 to the known samogenic acid, m. 270°; [α]23D -37°; di-Me ester, m. 147°. Both X and XII with alkaline N2H4.H2O gave IX. From all these results I was established as 1β,2β,3α-trihydroxy-5β- 25D-spirostan.

IT 547-01-3, Tokorogenin
(and cyclic 1,2-acetal with acetone and other derivs.)

RN 547-01-3 HCAPLUS

CN Spirostan-1,2,3-triol, (1β,2β,3α,5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



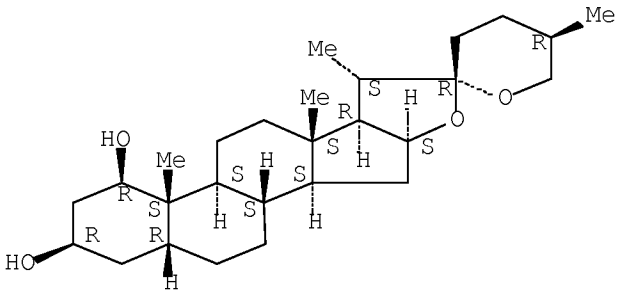
(and derivs., as structure for tokorogenin

IT 472-10-6P, 5β,25D-Spirostan-1β,3β-diol
6870-82-2P, 5β,25D-Spirostan-3-one, 1β,2β-dihydroxy-
RL: PREP (Preparation)
(preparation of)

RN 472-10-6 HCAPLUS

CN Spirostan-1,3-diol, (1β,3β,5β,25R)- (9CI) (CA INDEX NAME)

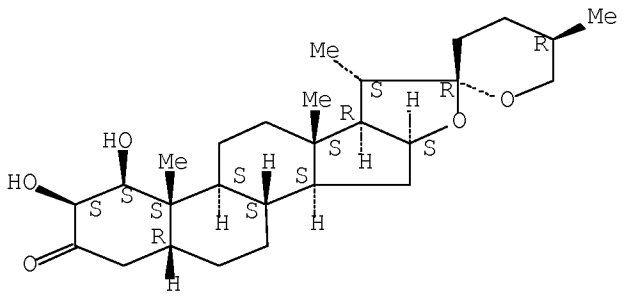
Absolute stereochemistry.



RN 6870-82-2 HCAPLUS

CN 5β-Spirostan-3-one, 1β,2β-dihydroxy-, (25R)- (8CI) (CA INDEX NAME)

Absolute stereochemistry.



L97 ANSWER 10 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1958:65895 HCAPLUS Full-text
DN 52:65895
OREF 52:11878e-i,11879a-g
TI Reduction of 4β,5-epoxysmilagenone and 4α,5-epoxytigogenone with lithium aluminum hydride
AU de Vivar, A. Romo; Ruelas, J. Perez; Romo, J.
SO Boletin del Instituto de Quimica de la Universidad Nacional Autonoma de Mexico (1957), 9, 59-72
CODEN: BIQUA5; ISSN: 0076-745X
DT Journal
LA Unavailable
OS CASREACT 52:65895
AB Oxidation of Δ4-diosgenone (I) with H2O2 in an alkaline medium yielded 2 isomeric epoxides, 4β,5-epoxysmilagenone (II), and 4α,5-epoxytigogenone (III). Reduction of II and III with LiAlH4 yielded 4 diols, 2 each from II and III. M.ps. were uncor., rotations determined at 23° in CHCl3. 2α-Acetoxydiosgenone (4 g.) in 30 ml. tetrahydrofuran (THF) added slowly to 1 g. LiAlH4 in 50 ml. Et2O, the mixture refluxed 1 hr., poured into H2O, acidified with dilute HCl, extracted with CHCl3, and the washed and dried extract evaporated yielded 2.2 g. 20α,22a-25D-spirost-4-ene- 2α,3β-diol (IV), m. 251-4°, [α]D -83.5°; diacetate (V), m. 209-11°, [α]D -136°. V (400 mg.) in 50 ml. EtOAc and 20 ml. AcOH hydrogenated over 80 mg. PtO2 and the mixture filtered and concentrated yielded 260 mg. gitogenin, m. 271-3°, [α]D -65°. I (10 g.) in 400 ml. EtOH treated simultaneously at room temperature with 3 g. KOH in 6 ml. H2O and 15 ml. 30% H2O2, the mixture held 45 min. at 30°, diluted with H2O, and filtered yielded 3.45 g. II, m. 211-12°, [α]D 20°. The mother liquors dissolved in hexane and chromatographed on Al2O3 yielded 350 mg. III, m. 210-11°, [α]D -125°. II (1 g.) in 20 ml. AcOH treated with 2 ml. H2SO4 in 10 ml. AcOH, the mixture held 1 hr. at room temperature, diluted with H2O, and filtered yielded 0.5 g. 4-hydroxydiosgenone (VI), m. 241-2°, [α]D -30°; acetate, m. 203-4° (Ac2O-pyridine), [α]D -13°. III (300 mg.) in 20 ml. AcOH treated with 1 ml. H2SO4 in 10 ml. AcOH yielded 125 mg. VI, m. 238-40°. VI (300 mg.) and 500 mg. o-C6H4(NH2)2 refluxed 2 hrs., diluted with H2O, and filtered yielded 140 mg. phenazine derivative, m. 247-9°, [α]D -61°. II (10 g.) in 70 ml. THF added slowly to 4 g. LiAlH4 in 100 ml. Et2O, the mixture refluxed 1 hr., decomposed with EtOH, poured into H2O, acidified with dilute HCl, and filtered yielded 3.45 g. 5-hydroxyepismilagenin (VII), m. 260-3°, [α]D -60°; 3-monoacetate (VIIa), m. 218-20° (Ac2O-pyridine), [α]D -45°. The mother liquors from VII evaporated to dryness, the residue (6.2 g.) heated 1 hr. on the steam bath with 30 ml. Ac2O and 30 ml. pyridine, diluted with H2O,

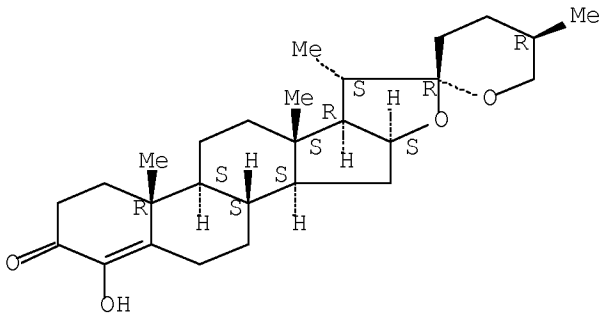
and filtered yielded 1.7 g. 3-acetate (VIII), m. 203-5°, of 5-hydroxyepismilagenin. The mother liquor chromatographed on Al2O3 and eluted with hexane yielded 3.16 g. 3-monoacetate (IX), m. 195-6°, [α]D -42°, of 5-hydroxysmilagenin. The end fractions yielded 440 mg. VIIa, m. 215-17°. IX (1 g.) in 100 ml. MeOH treated with 500 mg. K2CO3 in 8 ml. H2O, the mixture refluxed 1 hr., diluted with H2O, and filtered yielded 680 mg. 5-hydroxysmilagenin (X), m. 265-7°, [α]D -46°. X (880 mg.) dissolved in 50 ml. CHCl3, 15 ml. CHCl3 distilled, 3 ml. pyridine added, the mixture treated at 0° with 1 ml. SOCl2, held 3 hrs. at 0°, washed, and concentrated yielded 575 mg. cyclic sulfite (XI), m. 193-4°, [α]D -74°. X (300 mg.) in 15 ml. AcOH treated with 150 mg. CrO3 in 0.5 ml. H2O and 4 ml. AcOH, the mixture allowed to stand 1 hr. at room temperature, poured into H2O, and filtered yielded 80 mg. 5-hydroxysmilagenone (XIIa), m. 240-2°, [α]D -32°. VII (2 g.) in 40 ml. AcOH containing 750 mg. CrO3 yielded 1.2 g. XIIa, m. 240-2°. XIIa (300 mg.) in 30 ml. MeOH refluxed 1 hr. with 1 ml. HCl, diluted with H2O, and filtered yielded 230 mg. I, m. 188-90°, [α]D -19°. XIIa (400 mg.) in 30 ml. MeOH treated with 500 mg. KOH in 2 ml. H2O and the mixture refluxed yielded 250 mg. I, m. 183-5°. IX (1 g.) and 100 mg. p-MeC6H4SO3H in 25 ml. Ac2O held overnight at room temperature, the mixture poured into H2O, and filtered yielded 690 mg. diacetate (XIII), m. 208-10°, [α]D -55°. XIII (500 mg.) in 50 ml. MeOH containing 500 mg. KOH refluxed 9 hrs., diluted with H2O, and filtered yielded 380 mg. X, m. 248-52°. XIII (500 mg.) refluxed 1 hr. with 500 mg. K2CO3 was recovered. IX (1 g.) and 100 mg. p-MeC6H4SO3H in 40 ml. Ac2O processed as for VIII yielded 880 mg. diacetate (XIV), m. 248-50°, [α]D -66°. XIV (1.96 g.) refluxed 1 hr. in 250 ml. MeOH containing 1.5 g. KOH, the solution concentrated to 1/2 the original volume, diluted with H2O, and filtered yielded 1.585 g. 5-acetoxyepismilagenin (XV), m. 215-16°, [α]D 80°. XV (1.35 g.) in 60 ml. AcOH at room temperature treated with 500 mg. CrO3 in 10 ml. 80% AcOH, the mixture held 2 hrs. at room temperature, and processed as for XIIa yielded 930 mg. 5-acetoxysmilagenone (XVI), m. 213-15°, [α]D -49°. XVI with HCl or KOH yielded I, m. 180-3° and 185-7°, resp. III (400 mg.) in 10 ml. Et2O added slowly to 400 mg. LiAlH4 in 20 ml. Et2O, the mixture refluxed 30 min., poured into H2O, acidified with dilute HCl, and extracted with CHCl3 yielded 110 mg. 5-hydroxytigogenin (XVII), m. 265-7°, [α]D -50°. XVII (1 g.) in 20 ml. oxidized with 350 mg. CrO3 in 6 ml. 80% AcOH yielded 660 mg. 5-hydroxytigogenone (XVIII), m. 278-80°, [α]D -60°. 5-Hydroxyepitigogenin (60 mg.) in 3 ml. AcOH treated with 30 mg. CrO3 in 3 ml. 80% AcOH yielded 16 mg. XVIII, m. 273-5°. XVIII with HCl yielded I, m. 182-4°. The monoacetate (1 g.) treated with Ac2O and p-MeC6H4SO3H and the product chromatographed on Al2O3 yielded 510 mg. 5-hydroxytigogenin diacetate (XIX), m. 195-6°, [α]D -64°. XIX (300 mg.) refluxed 1 hr. in 20 ml. MeOH containing 500 mg. KOH yielded 265 mg. 5-acetoxytigogenin (XX), m. 210-11°, [α]D -62°. XX (250 mg.) in 10 ml. AcOH oxidized with 150 mg. CrO3 in 5 ml. 80% AcOH yielded 135 mg. 5-acetoxytigogenone (XXI), m. 218-19°, [α]D -78°. Dehydration with HCl yielded I, m. 183°. I (4 g.) in 70 ml. CHCl3 treated with 4 g. (BzO)2 in 100 ml. CHCl3, the mixture held 72 hrs. at 4°, washed, and the solvent evaporated yielded 2.1 g. 5,6α-epoxytigogenin (XXII), m. 222-3°, [α]D -118°; acetate, m. 236-7° (Ac2O-pyridine 1 hr. on the steam bath), [α]D -122°. XXII (1.3 g.) in 15 ml. THF added to 800 mg. LiAlH4 in 60 ml. Et2O, the mixture refluxed 3 hrs., poured into H2O, acidified with dilute HCl, heated slightly to evaporate the Et2O, then filtered yielded 900 mg. XVII, m. 264°; acetate, m. 242-3°.

IT 13944-32-6P, Diosgenone, 4-hydroxy-, phenazine derivative, acetate
119008-61-6P, 20α,22a,25D-Spirost-4-ene-2α,3β-diol
RL: PREP (Preparation)
(preparation of)

RN 13944-32-6 HCAPLUS

CN Spirost-4-en-3-one, 4-hydroxy-, (25R)- (8CI, 9CI) (CA INDEX NAME)

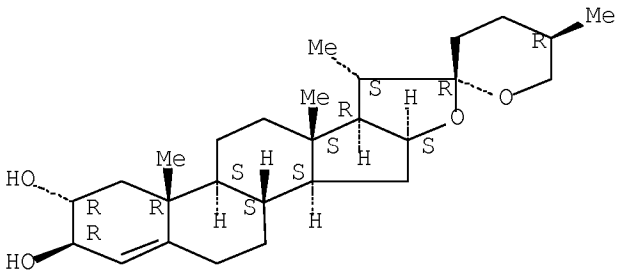
Absolute stereochemistry.



RN 119008-61-6 HCAPLUS

CN 20α,22α,25D-Spirost-4-ene-2α,3β-diol (6CI) (CA INDEX NAME)

Absolute stereochemistry.



IT 262437-80-9, Aluminum lithium hydride
(reduction with, of 4β,5-epoxysmilagenone and 4α,5-epoxytigogenone)

RN 262437-80-9 HCAPLUS

CN Aluminum lithium hydride (CA INDEX NAME)

Component	Ratio	Component Registry Number
H	x	12385-13-6
Li	x	7439-93-2
Al	x	7429-90-5

L97 ANSWER 11 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN

AN 1955:77946 HCAPLUS Full-text

DN 49:77946

OREF 49:14785h-i,14786a-f

TI Constitution and stereochemistry of samogenin, markogenin, and mexogenin

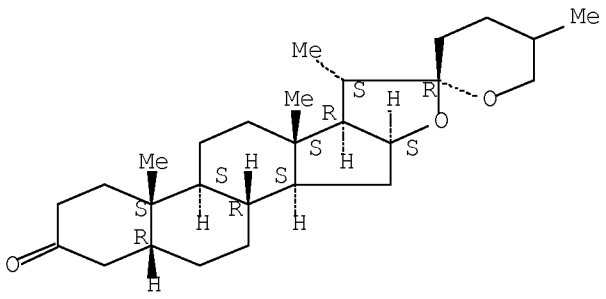
AU Djerassi, Carl; Fishman, Jack; Moore, James A.

CS Wayne Univ., Detroit, MI

SO Chemistry & Industry (London, United Kingdom) (1954) 1320-2
CODEN: CHINAG; ISSN: 0009-3068

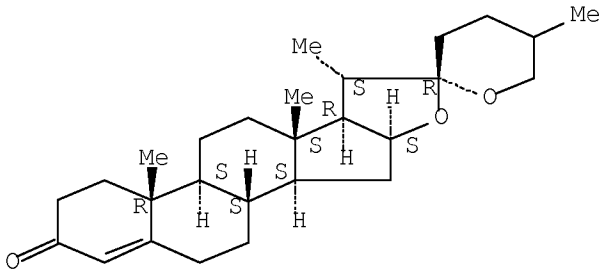
DT Journal
LA Unavailable
AB Samogenin (I) was converted to the dimesylate (II), C29H48O8S2, m. 201-2° (all m.ps. uncorr.), [α]28D -63° (all rotations in CHCl3). II with NaI in Me2CO gave an olefin (III), C27H22O2, m. 149-50°, [α]26D -84°. Reduction of III with Pt oxide in EtOH yielded 22a-spirostan (IV), C27H44O2, m. 139-40°, [α]25D -75°, also obtained by Wolff-Kishner reduction of 3-oxo-22a-spirostan, which in turn had been derived from diosgenin (C.A. 47, 8761d). This constitutes the 1st rigorous correlation of I with a known sapogenin and establishes the stereochemistry of all asymm. centers with the exception of the 2 vicinal OH groups. I readily forms an acetonide, C30H48O4, m. 167-70°, [α]29D -72°, under conditions where gitogenin (2α,3β-dihydroxy-5α,22a- spirostan) was recovered, indicating that I is a cis glycol. This was confirmed when III was treated with OsO4; the resulting glycol, m. 205-7°, [α]D -88°, (diacetate, m. 196-8°, [α]D -75°), was identical with the natural sapogenin. This indicates that I is a cis glycol of the 5β ("normal") series with the OH groups located most probably at positions 2 and 3 or 3 and 4. A differentiation between these 2 alternatives was accomplished in the following manner. Wolff-Kishner reduction of 3-oxo-22a-spirost-4-ene (diosgenone) gave 3 olefins, C27H42O2, separable by chromatography: (a) 22a-spirost-4-ene, m. 134-5° and 144-6°, [α]23D -30°, also obtained by Raney Ni desulfurization of diosgenone cycloic ethylene mercaptal, C29H44O2S2, m. 265-7°, [α]25D 30°; (b) 5α,22a-spirost-3-ene, m. 172-4°, [α]25D -34°, converted by catalytic hydrogenation to 5α,22a-spirostan and by BzO2H oxidation to the corresponding 3α,4α-oxide, C27H42O3, m. 195-8°, [α]22D -60°, the structure of which was demonstrated by LiAlH4 reduction to epitigogenin (3α-hydroxy- 5α,22a-spirostan); and (c) an olefin which was assigned the structure 22a-spirost-3-ene (V), m. 142.5-44°, [α]25D -86°, since it was hydrogenated readily to IV. OsO4 hydroxylation of V yielded the corresponding 3ξ,4ξ(cis)-dihydroxy-22a-spirostan (VI), C27H44O4, m. 192-5°, [α]29D -82° (diacetate, m. 210-12°, [α]29D -46°), which was oxidized with CrO3 to the derived 3,4-seco acid (VII), C27H42O6, m. 264-6°, [α]27D -19° (C5H5N) [di-Me ester (VIII), m. 195-7°, [α]25D -47°]. VII and VIII were not identical to the corresponding oxidation products of I, samogenic acid, m. 270-3°, [α]27D -39° (C5H5N), and di-Me samogenate (IX), m. 145-7°, [α]22D -32°, thus excluding a 3,4-di-HO structure for I. 3α-Hydroxy-22a-spirostan tosylate, C34H50O5S, m. 168-70°, [α]29D -38°, yielded a mixture of the Δ2- and Δ3-olefins, III and V, when refluxed with collidine. OsO4 hydroxylation of this product, followed by chromatographic separation, furnished I and VI. In a 2nd experiment, the hydroxylation product was not purified but rather converted by CrO3 oxidation, CH2N2 methylation, and chromatography into VIII and IX. This reduces the structural possibilities for I to 2α,3α- and 2β,3β-dihydroxy- 22a-spirostan with the same configuration in the side chain as diosgenin. Since markogenin (X) affords a pseudo derivative, different from that derived from I, but can be isomerized by strong acid to I, it follows that X differs from I only in the configuration at C-25 and possibly also at C-22. The same configuration for the HO groups has been demonstrated previously. Since mexogenin yields I on Wolff-Kishner reduction , it must be x-oxo-22a-spirostan-2α,3α- or 2β,3β-diol. This group of 2,3-dihydroxy-5β-sapogenins represents the 1st example of naturally occurring cis glycols in the sapogenin series.
IT 639-95-2, 5β,22a-Spirostan-3-one
(Wolff-Kishner reaction with)
RN 639-95-2 HCAPLUS
CN Spirostan-3-one, (5β)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



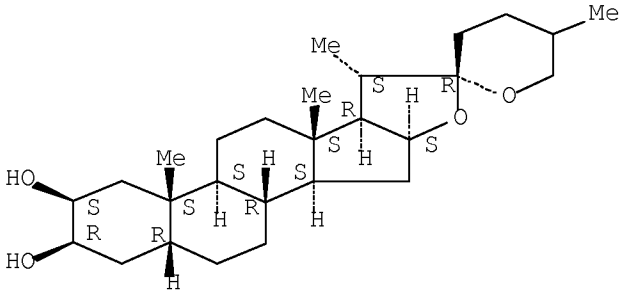
IT 7662-01-3, 22a-Spirost-4-en-3-one
(Wolff-Kishner reaction with, and cyclic ethylene mercaptole and other derivs.)
RN 7662-01-3 HCAPLUS
CN Spirost-4-en-3-one (9CI) (CA INDEX NAME)

Absolute stereochemistry.



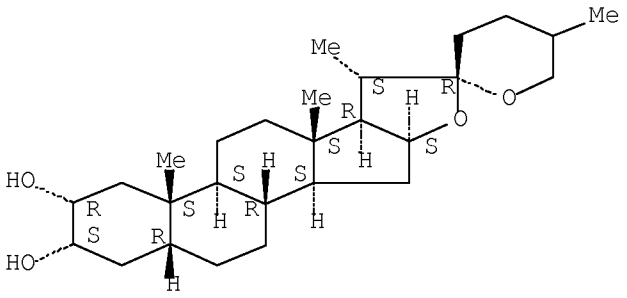
IT 911458-95-2, 5β,22a-Spirostan-2β,3β-diol
911459-00-2, 5β,22a-Spirostan-2α,3α-diol
(and derivs.)
RN 911458-95-2 HCAPLUS
CN 5β,22a-Spirostan-2β,3β-diol (5CI) (CA INDEX NAME)

Absolute stereochemistry.



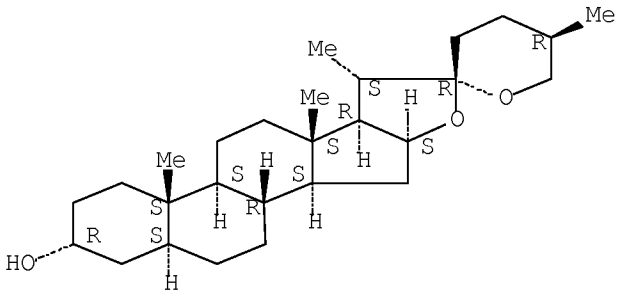
RN 911459-00-2 HCAPLUS
CN 5β,22a-Spirostan-2α,3α-diol (5CI) (CA INDEX NAME)

Absolute stereochemistry.



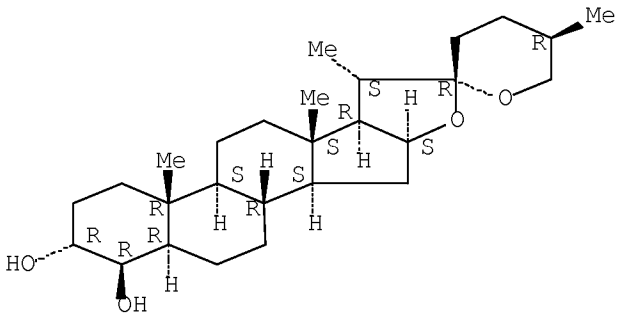
IT 6788-40-5P, Epitigogenin 61010-49-9P, 22a-Spirostan-3ξ,4ξ-diol 911453-64-0P, 5α,22a-Spirostan-3α-ol
RL: PREP (Preparation)
(preparation of)
RN 6788-40-5 HCAPLUS
CN Spirostan-3-ol, (3α,5α,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



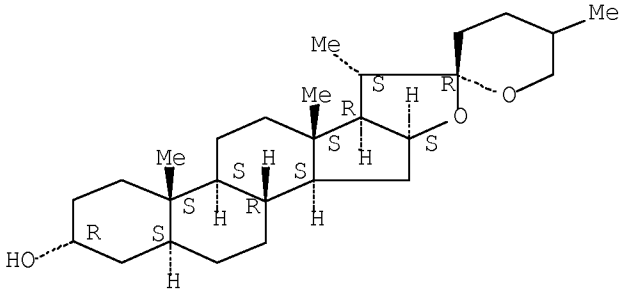
RN 61010-49-9 HCAPLUS
CN Spirostan-3,4-diol, (3α,4β,5α,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



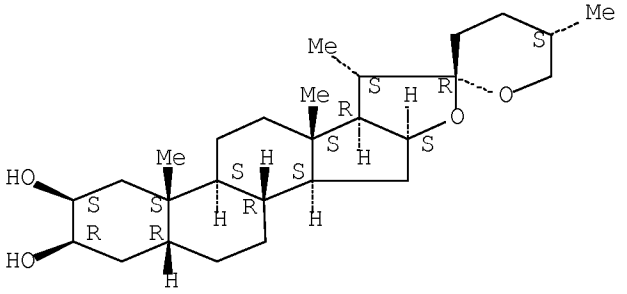
RN 911453-64-0 HCAPLUS
CN 5α,22a-Spirostan-3α-ol (5CI) (CA INDEX NAME)

Absolute stereochemistry.



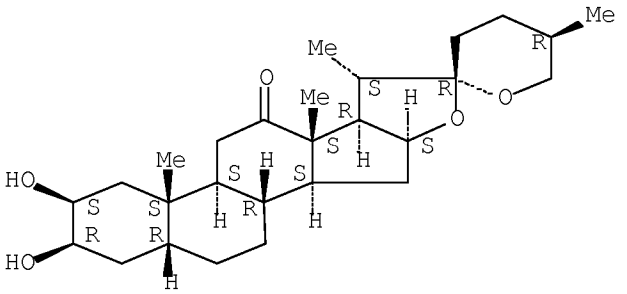
IT 562-35-6, Markogenin 16680-64-1, Mexogenin
(stereochemistry of)
RN 562-35-6 HCAPLUS
CN Spirostan-2,3-diol, (2β,3β,5β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



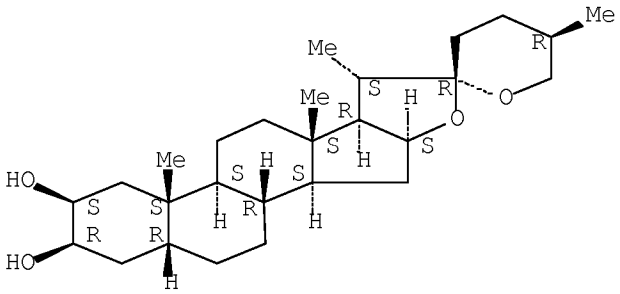
RN 16680-64-1 HCAPLUS
CN Spirostan-12-one, 2,3-dihydroxy-, (2β,3β,5β,25R)- (9CI)
(CA INDEX NAME)

Absolute stereochemistry.



IT 469-97-6, Samogenin
(stereochemistry of, and cyclic acetal with acetone and other derivs.)
RN 469-97-6 HCAPLUS
CN Spirostan-2,3-diol, (2β,3β,5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L97 ANSWER 12 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1955:49607 HCAPLUS Full-text
DN 49:49607
OREF 49:9685g-i,9686a-i,9687a-g
TI Synthesis of cortisone. VIII. Wagner-Meerwein rearrangement involving rings C and D of the steroid nucleus
AU Elks, J.; Phillipps, G. H.; Taylor, D. A. H.; Wyman, L. J.
CS Natl. Inst. Med. Research, London
SO Journal of the Chemical Society (1954) 1739-49
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable
AB cf. C.A. 49, 2470i. Hecogenin acetate (I) (100 g.) and 100 g. p-MeC6H4SO2NHNH2 (II), in 7 l. EtOH refluxed 65 hrs. gave 100 g. (74%) crude hecogenin acetate p-toluenesulfonylhydrazone (III); m. 274° (decomposition) (from EtOH-CHCl3), [α]D -15° (all rotations determined in CHCl3 unless otherwise stated), λEtOHmax. 226 mμ (ε 11600), νmaximum (CS2) 3250, 1732, 1245, 1342, 1160, 977, 914, 897, and 860 cm.-1 In another experiment with 36 g. I, 18.6, 24.9, and 31.1 g. III were deposited after 6, 24, and 50 hrs. I (20 g.) in CHCl3 added to 10 g. II in EtOH and concentrated HCl gave 23 g. (85%) III. I (2 g.) in HOAc treated 1 hr. with 2 g. II yielded 2.4 g. (89%) III. III (50 g.) heated gradually to 130-40° with 15 g. Na in 1 l. (CH2OH)2 until no further gas evolution was apparent, and the mixture cooled, diluted with H2O, and left overnight yielded on crystallization 21.4 g. of a free alc. (IV), m. 125-33°. IV on acetylation yielded 19.5 g. (55%) "compound A" (V), m. 142-5° (from aqueous MeOH), [α]D -57°, νmaximum (CS2) 1733, 1238, 980, 920, 898 and 860 cm.-1 Purified IV, obtained by hydrolysis of V with alc. KOH, m. 120-5°, [α]D -55°, νmaximum (Nujol) 3400, 983, 920, 898 and 865 cm.-1 The mother liquor from III yielded 1.2 g. solid which on acetylation yielded 0.94 g. 3β-acetoxy-5α,22a-spirost-11-ene (VI), m. 206-11°. An alternative method of isolating V was by acetylating the crude reaction product, followed by chromatography. III (28 g.) refluxed 0.5 hr. with 3 g. Na in 800 ml. BuOH and the crude product fractionally crystallized yielded 9.18 g. (51%) IV and 2.1 g. (12%) 5α,22a-spirost-11-en-3β-ol (VII), tablets, m. 192-4°, [α]D -37°. VII on acetylation yielded VI, [α]D -43°. Acetylation of the solid obtained from the combined mother liquors gave 2.6 g. VI (total yield, 25%). The mother

liquor yielded a solid which on chromatography gave 700 mg. (3.5%) 3β-acetoxy-C-nor-D-homo-5α,22a-spirost-17a-ene (VIII), m. 215°, [α]D -81°. V (0.912 g.) in CCl4 treated at -25° with 320 mg. Br in CCl4, and the solution warmed up to 0°, then washed with H2O, NaHCO3 solution, and H2O, yielded 0.81 g. (66%) of the dibromide (IX), m. 108° (decomposition), [α]D -33°, νmaximum (CS2) 1735, 1240, 988, 918, 898, 860, and 702 cm.-1 IX decomposed when kept at room temperature or on attempted crystallization Tigogenin acetate (X) (0.5 g.) in HOAc hydrogenated at room temperature and pressure with 200 mg. PtO2 took up 1 mole H in 1 hr. and the residue on acetylation yielded 0.11 g. X, m. 204-7°, [α]D -72°, and 0.2 g. 3β,26-diacetoxy-5α,22a-furostan (XI), m. 114-16°, [α]D -14°, νmaximum (CS2) 1732 and 1240 cm.-1 The bands characteristic of the 22a-spirostan system were almost absent. XI hydrolyzed with alkaline KOH yielded 3β,26-dihydroxy-5α,22a- furostan, m. 165-7°, [α]D -6°, νmaximum (Nujol) 3300 cm.-1 V (5 g.) in CHCl3 left 0.5 hr. with 15 ml. 2.8N o-HO2CC6H4CO3H in Et2O at room temperature and the crude product chromatographed on Al2O3 yielded 1.06 g. (21%) epoxide P (XII), m. 189-90°, [α]D -66°, νmaximum (CS2) 1732, 1240, 980, 918, 895, and 860 cm.-1, and 2.01 g. (39%) epoxide Q (XIII), m. 194-5°, [α]D -63°, νmaximum (CS2) 1734, 1240, 980,918,895, and 860 cm.-1 The infrared spectra of XII and XIII are quite different in detail. XII (0.5 g.) in 50 ml. tetrahydrofuran refluxed 3.5 hrs. with 0.5 g. LiAlH4 and the crude product acetylated yielded 41 mg. starting material and 0.383 mg. (76%) diol monoacetate (XIV), prisms, m. 192-4°, [α]D -63°, νmaximum (CS2) 3620, 1732, 1240, 978, 918, 898, and 860 cm.-1 XIV (100 mg.) left 2 hrs. at room temperature in 2 ml. C5H5N with 0.5 ml. POCl3 yielded 51 mg. V. XIII (0.5 g.) similarly reduced with LiAlH4 5 hrs. and the crude product acetylated yielded 0.306 g. (61%) of a diol monoacetate (XV), prisms, m. 161°, resolidified in needles, and finally m. 170-1°, [α]D -53° (c 1.4, Me2CO), νmaximum (CS2) 3600, 1735, 1240, 980, 916, 897, and 860 cm.-1 XV (0.155 g.) in 2 ml. C5H5N similarly dehydrated with POCl3 gave 0.092 g. V. V (1.6 g.) in Et2O containing 0 7 C5H5N left 65 hrs. with 1 g. OsO4, the Et2O removed, the residue refluxed 4.5 hrs. with 7 g. Na2SO3 in EtOH and H2O, and the crude product acetylated yielded 1.18 g. (69%) of a triol monoacetate (XVI), m. 214-17°, [α]D -40°, νmaximum (CS2)3620, 1732, 1240, 978, 918, 896, and 860 cm.-1 XVI was hydrolyzed to the free triol (XVII), prisms, m. 229-33°, [α]D -40°, νmaximum (CS2) 3350, 982, 918, 900, and 860 cm.-1 XVII (0.46 g.) in MeOH left 2 days at room temperature with 5 ml. 10% aqueous HIO4 yielded 0.28 g. (61%) of a diketone (XVIII), m. 157-60°, [α]D -21°, νmaximum (CS2) 3620, 1740, and 1714 cm.-1 XVIII gave a violet color with Na nitroprusside, showing the presence of a Me ketone grouping. I (10 g.) in EtOH and CH2Cl2 left 3 days at room temperature with 0.6 g. NaBH4 in 5 ml. H2O gave 4.2 g. (42%) 3β-acetoxy-5α,22a-spirostan-12β-ol (XIX), m. 211-16°, contaminated with the 12α-HO isomer. XIX (4 g. crude) added to 3 ml. MeSO2Cl in 13 ml. C5H5N at 0°, left overnight at room temperature, the crude product refluxed 2 hrs. with 100 ml. MeOH, the solution evaporated to dryness, and the residue hydrolyzed by refluxing 0.5 hr. with 4% KOH in 80% EtOH yielded 1.03 g. IV. The mother liquor from IV evaporated to dryness, and the residue reacetylated and chromatographed gave 800 mg. V and 1.26 g. 3β-acetoxy-12α-methanesulfonyloxy-5α,22a-spirostan (XX), m. 186-8°, [α]D -21°. The mother liquor from XX gave upon chromatography of the solid 75 mg. VIII. I (5 g.) in 25 ml. tetrahydrofuran refluxed 1 hr. with 0.8 g. LiAlH4 in 25 ml. tetrahydrofuran and the crude product acetylated yielded after chromatography 10% 3β,12α-diacetoxy-5α,22a- spirostan (XXI), prisms from aqueous MeOH, m. 153-6°, [α]D -17° (Me2CO, c 1), νmaximum (CS2) 1738, 1240, 976, 918, 895, and 860 cm.-1 XXI was hydrolyzed with EtOH-KOH to the free diol (XXII), m. 200-6°, [α]D -30° (Me2CO), νmaximum (Nujol) 3600, 3450, 981, 919, 903, and 863 cm.-1 The chromatogram also yielded 45% 3β,12β-diacetoxy-5α,22a-spirostan (rockogenin

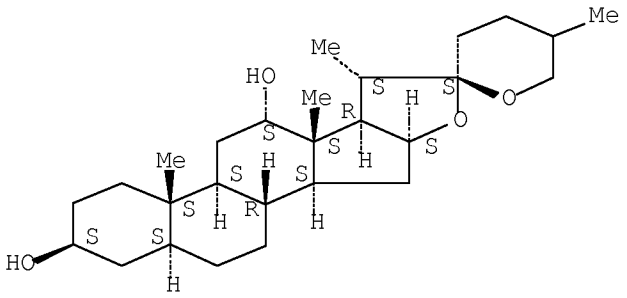
diacetate) (XXIII), m. 198-203°, [α]D -68° (c 1, CHCl3), -63° (Me2CO), νmaximum (CS2) 1735, 1240, 978, 918,898, and 860 cm.-1 XXIII similarly yielded the free diol (XXIV), m. 216-19°, [α]D -60° (Me2CO), νmaximum (Nujol) 3300, 973, 914, 892, and 860 cm.-1 XXI (0.75 g.) refluxed 2 hrs. with 0.225 g. KHCO3 in 24 ml. MeOH and 6 ml. H2O gave 585 mg. (85%) crude 12α-acetoxy-5α,22a- spirostan-3β-ol (XXV) (pure, m. 231-3°), [α]D -15°, νmaximum (CS2) 3620, 1739, 1240, 978, 920, 898, and 860 cm.-1 XXV (0.55 g.) in 15 ml. HOAc left at room temperature 4 hrs. with 1.5 equivs. CrO3 gave 0.5 g. (91%) 12α-acetoxy-5α,22a-spirostan-3-one (XXVI), m. 214-17°, [α]D 1°, νmaximum (CS2) 1739, 1237, 1715, 981, 920, 899, and 863 cm.-1. XXVI was saponified with MeOH-KOH to 12α-hydroxy-5α,22a-spirostan-3-one, m. 254-7°, [α]D -30°, νmaximum (CS2) 3620, 1712, 979, 917, and 895 cm.-1 IV (1 g.) in HOAc left at room temperature 4 hrs. with 17 ml. 0.55N CrO3 yielded a ketone, m. 101-4°, [α]D -40°, νmaximum (CS2) 1715, 980, 920, 900, and 860 cm.-1; 2,4-dinitrophenylhydrazone, orange solid, m. 206-8°. 3β-Acetoxy-12α,23-dibromo-5α,22a- spirostan-11β-ol (3 g.) refluxed 3.5 hrs. with 30 g. Zn in 300 ml. HOAc yielded 1.68 g. (78%) VI, νmaximum (CS2) 1732, 1240, 978, 918, 895, and 860 cm.-1, also obtained in 30% yield from 3β-acetoxy-23-bromo- 11β,12β-epoxy-5α,22a-spirostan. The free alc., VII, obtained by hydrolysis of VI, νmaximum (Nujol) 3560, 3330, 978, 918, 900, and 861 cm.-1 VII like VI showed bands of medium intensity at 702 and 760 cm.-1, with a shoulder at 3000 cm.-1, indicative of a cis-1,2- disubstituted ethylene grouping. VI (200 mg.) in 6 ml. CHCl3 left overnight in the refrigerator with 0.5 ml. 2.8N o-HO2CC6H4CO3H yielded 155 mg. (75%) 3β-acetoxy-11α,12α-epoxy- 5α,22a-spirostan (XXVII), needles, m. 221-5°, [α]D -49.5°, νmaximum (CS2) 1735, 1240, 978, 918, 895, and 860 cm.-1 There was no indication of the presence of the isomeric 11β,12β-epoxide. XXVII (0.5 g.) refluxed 2 hrs. with 0.6 g. LiAlH4 in 25 ml. tetrahydrofuran yielded XXII. Crude XXII was acetylated to XXI, identical with the specimen prepared from I. XXI was obtained in 44% yield from XXVII. XXII (200 mg., crude) in 7 ml. HOAc left at room temperature 4 hrs. with CrO3 gave hecogenone (XXVIII), plates, m. 232-5°, [α]D 21°, νmaximum (CS2) 1710, 978, 918, 896, and 860 cm.-1, identical with a sample prepared from rockogenin by the same method. 3β-Acetoxy-5α,22a-spirostan-12β-ol (rockogenin monoacetate) (XXIX), prepared by a method mentioned above, m. 214-19°, [α]D -65° (CHCl3), -61° (dioxane), νmaximum (CS2) 3620, 1736, 1238, 978, 918, 895, and 862 cm.-1 XXIX with MeSO2Cl yielded a solid, m. 125-30° (decomposition), which, refluxed 4 hrs. with 1.5 g. K in 100 ml. tert-BuOH, gave 2.8 g. (73%) 3β-hydroxy-C-nor-D-homo-5α,22a-spirost-17-ene (XXX), m. 157-69°, [α]D -66.5°, νmaximum 1642, 886, 980, 920, 898, and 864 cm.-1 The presence of an OH group was shown by the spectrum of a Nujol mull, with maximum at 3500 and 3280 cm.-1 XXX yielded VIII, νmaximum 1732, 1238, 1638, 884, 978, 918, 896, and 862 cm.-1 The structure of compound A (V) is discussed in the light of both its reactions and the stereochem. requirements of the rearrangement.

IT 884309-78-8, 5α,22a-Spirostan-3β,12α-diol
(and esters)

RN 884309-78-8 HCAPLUS

CN 5α,22a-Spirostan-3β,12α-diol (5CI) (CA INDEX NAME)

Absolute stereochemistry.

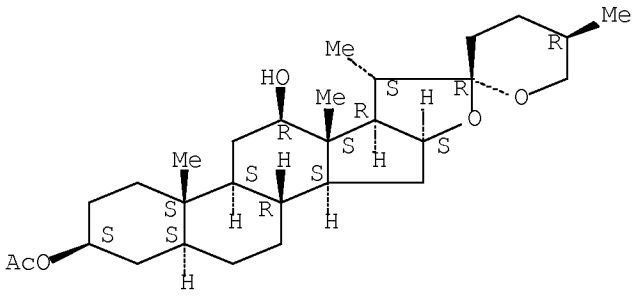


IT 863-85-4P, Rockogenin, acetate 2137-20-4P, Hecogenone 16653-52-4P, Rockogenin 119065-01-9P, 5α,22a-Spirost-11-en-3β-ol 120964-63-8P, 5α,22a-Spirost-11-en-3β-ol, acetate 884310-29-6P, 5α,22a-Spirostan-3β,12β-diol 911442-63-2P, Methanesulfonic acid, 12-ester with 5α,22a-spirostan-3β,12α-diol 3-acetate 911460-03-2P, 5α,22a-Spirostan-3-one, 12α-hydroxy-, acetate 911460-08-7P, 5α,22a-Spirostan-3-one, 12α-hydroxy-
RL: PREP (Preparation)
(preparation of)

RN 863-85-4 HCAPLUS

CN Spirostan-3,12-diol, 3-acetate, (3β,5α,12β,25R)- (9CI) (CA INDEX NAME)

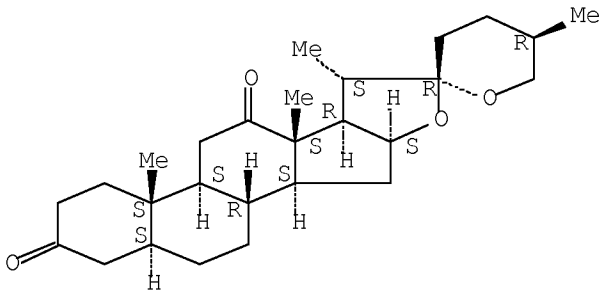
Absolute stereochemistry.



RN 2137-20-4 HCAPLUS

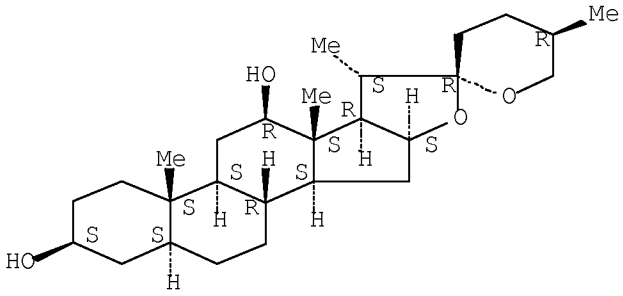
CN Spirostan-3,12-dione, (5α,25R)- (CA INDEX NAME)

Absolute stereochemistry.



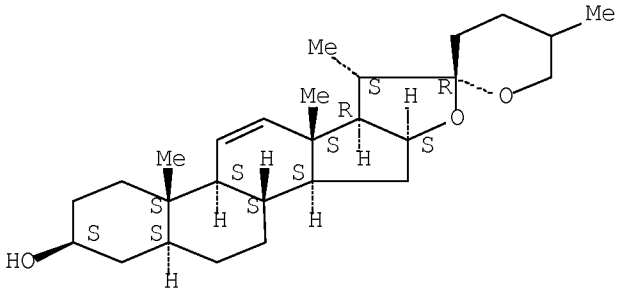
RN 16653-52-4 HCAPLUS
CN Spirostan-3,12-diol, (3β,5α,12β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



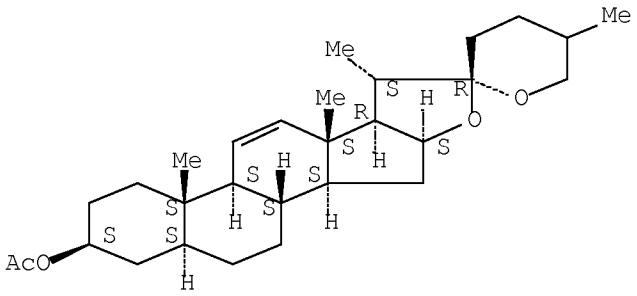
RN 119065-01-9 HCAPLUS
CN 5α,22α-Spirost-11-en-3β-ol (6CI) (CA INDEX NAME)

Absolute stereochemistry.



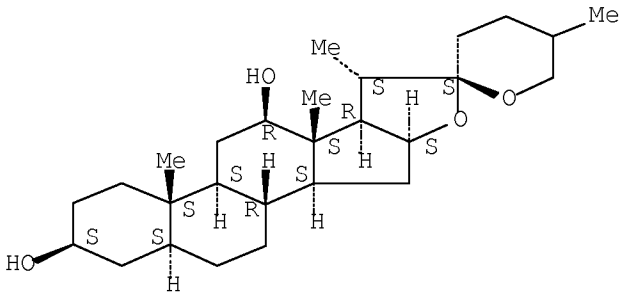
RN 120964-63-8 HCAPLUS
CN 5α,22a-Spirost-11-en-3β-ol, acetate (6CI) (CA INDEX NAME)

Absolute stereochemistry.



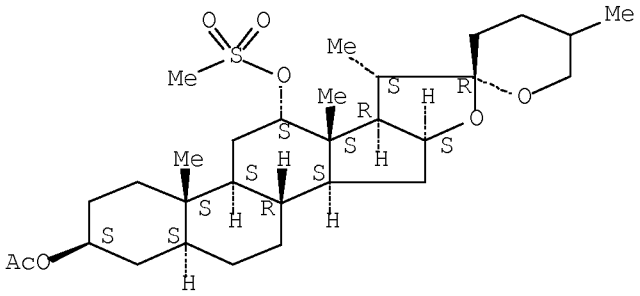
RN 884310-29-6 HCAPLUS
CN 5α,22a-Spirostan-3β,12β-diol (5CI) (CA INDEX NAME)

Absolute stereochemistry.



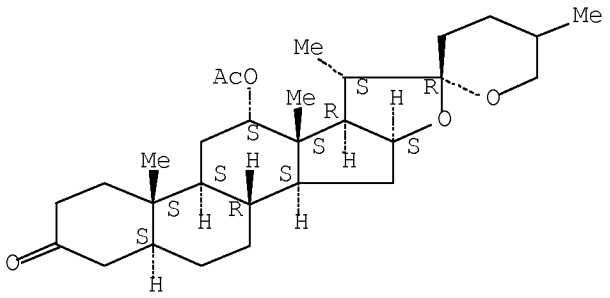
RN 911442-63-2 HCAPLUS
CN Methanesulfonic acid, 12-ester with 5α,22a-spirostan-3β,12α-diol 3-acetate (5CI) (CA INDEX NAME)

Absolute stereochemistry.



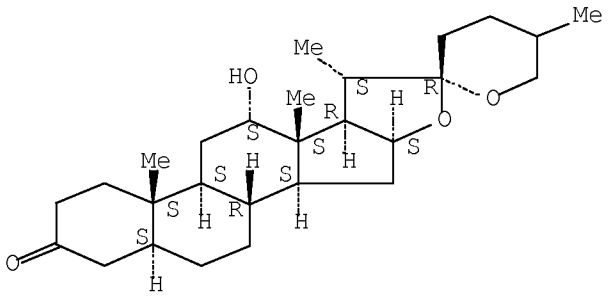
RN 911460-03-2 HCAPLUS
CN 5α,22a-Spirostan-3-one, 12α-hydroxy-, acetate (5CI) (CA INDEX NAME)

Absolute stereochemistry.



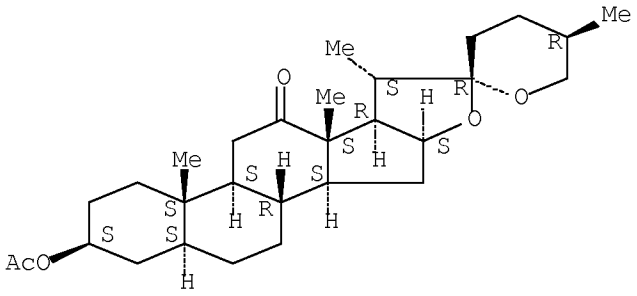
RN 911460-08-7 HCAPLUS
CN 5α,22a-Spirostan-3-one, 12α-hydroxy- (5CI) (CA INDEX NAME)

Absolute stereochemistry.



IT 915-35-5, Hecogenin, acetate
(spectrum of)
RN 915-35-5 HCAPLUS
CN Spirostan-12-one, 3-(acetyloxy)-, (3β,5α,25R)- (CA INDEX NAME)

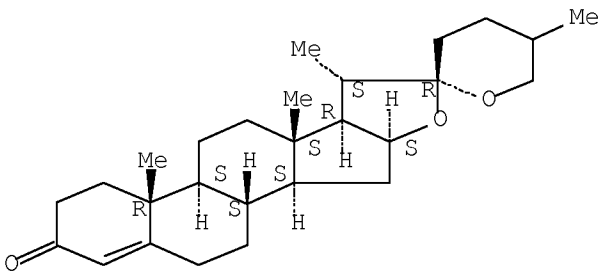
Absolute stereochemistry.



L97 ANSWER 13 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1955:8351 HCAPLUS Full-text
DN 49:8351
OREF 49:1758g-i,1759a-e
TI Steroids. L. The oxidation of steroidal allylic alcohols with manganese dioxide. A novel synthesis of testosterone

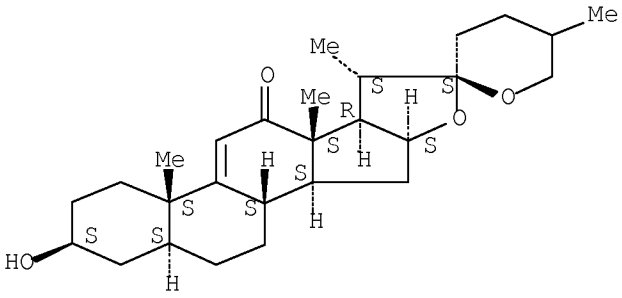
AU Sondheimer, Franz; Amendolla, C.; Rosenkranz, G.
CS Syntex, S.A., Mexico City, Mex.
SO Journal of the American Chemical Society (1953), 75, 5930-2
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
OS CASREACT 49:8351
AB cf. C.A. 48, 12157a. The oxidation of a number of steroidal allylic alcs. to the corresponding CO compds. with MnO2 is described. 4-Androstene-3,17- dione (I) reduced with LiAlH4 gave a mixture of 4-androstene-3β,17β-diol (II) and the 3α,17β-diol (III) which was oxidized with MnO2 in 90% over-all yield to testosterone (IV). Similarly progesterone (V) was converted to 4-pregnen-20β-ol-3- one (VI). The MnO2 used in the oxidns. described was prepared from KMnO4 and MnSO4 as previously described (C.A. 48, 6386b). 4-Cholesten-3β- ol, m. 129-31°, [α]D20 45°, in 100 cc. CHCl3 shaken 24 h. at room temperature with 10 g. MnO2 showed that the maximum at 240 mμ remained essentially unchanged and that an addnl. maximum at 284 mμ (log ε 3.17) appeared. A similar run shaken 3 h., and the resulting product recrystd. from MeOH yielded 0.93 g. (93%) 4-cholesten-3-one, m. 78-9°, λmaximum 240 mμ (log ε 4.22). A mixture of 22a-spirost-4-en-3β-ol and the Δ4-3α-ol, m. 181-3°, obtained by the reduction of 22a-spirost-4-en-3-one, which with LiAlH4 shaken in 150 cc. CHCl3 with 15 cc. MnO2 4 h. at room temperature, the mixture filtered, and the product recrystd. from CHCl3-Et2O yielded 1.26 g. (84%) 22a-spirost-4-en-3-one, m. 183-5°, [α]D20 -6, λmaximum 240 mμ (log ε 4.24); the rotations were measured in CHCl3 and the ultra-violet absorption spectra in 95% EtOH. 22a-Spirost-5-en-3β,7α-diol 3-acetate (0.50 g.), m. 190-3°, [α]D20 -155°, in 50 cc. C6H6 shaken 24 h. at room temperature with 5 g. MnO2, and the crystalline product [λmaximum 234 mμ (log ε 4.10)] recrystd. from MeOH yielded 0.29 g. (58%) 22a-spirost-5-en-3β-ol-7-one acetate, m. 198-9°, [α]D20 -158°, λmaximum 234 mμ (log ε 4.18), νmax. 1726, 1674 cm.-1 5α,22a-Spirost-9(11)-ene-3β,12-diol, m. 200-3°, (most probably a mixture of C-12 stereoisomers) in 50 cc. CHCl3 shaken 10 h. at room temperature with 5 g. MnO2, and the product [λmaximum 238 mμ (log ε 4.07)] recrystd. from CHCl3-Me2CO yielded 0.38 g. (76%) 5α,22a-spirost-9(11)-en-3β-ol-12-one, m. 221-3°, λmaximum 238 mμ (log ε 4.16), νmax. 1718, 1670 cm.-1 I (50 g.) in 300 cc. dry tetra-hydrofuran added with stirring and cooling to 15 g. LiAlH4 in 1.5 l. THF during 0.5 h., the excess LiAlH4 destroyed with EtOAc and concentrated aqueous Na2SO4, the mixture treated with 100 g. solid Na2SO4 and filtered, the filter residue washed with THF, and the solution evaporated yielded 50.4 g. mixture of II and III, m. 165-71°. The mixture ground in a mortar, suspended in 1250 cc. CHCl3, stirred 10 h. at room temperature with 250 g. MnO2, and filtered, the filter residue washed with hot CHCl3, the combined filtrate and washing evaporated to dryness, and the residue recrystd. from Me2CO-hexane yielded 38.2 g. IV, m. 152-3°, [α]D20 108°, λmaximum 240 mμ (log ε 4.23), 6.9 g. 2nd crop, m. 150-2°, and 3rd crops totaling 45.1 g. (90%). V (5.0 g.) reduced in the usual manner with LiAlH4, the reduction product (5.0 g.), m. 162-72°, in 500 cc. CHCl3 stirred 24 h. at room temperature with 50 g. MnO2, and the product recrystd. from Et2O-pentane gave 3.3 g. (66%) VI, m. 166-8°; recrystd., m. 174-5°, [α]D20 86°, λmaximum 240 mμ (log ε 4.23), λmax.CHCl3 1660 cm.-1; acetate, m. 161-2° (from Me2CO-hexane), [α]D20 134°, λmaximum 240 mμ (log ε 4.22), νmax. 1718, 1660 cm.-1
IT 7662-01-3P, 22a-Spirost-4-en-3-one 882741-52-8P, 5α,22a-Spirost-9(11)-en-12-one, 3β-hydroxy-
RL: PREP (Preparation)
(preparation of)
RN 7662-01-3 HCAPLUS
CN Spirost-4-en-3-one (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 882741-52-8 HCAPLUS
CN INDEX NAME NOT YET ASSIGNED

Relative stereochemistry.



L97 ANSWER 14 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1954:3641 HCAPLUS Full-text
DN 48:3641
OREF 48:699f-i,700a-b
TI Steroids. XL. The oxidation of unsaturated steroidal alcohols with manganese dioxide
AU Sondheimer, F.; Rosenkranz, G.
CS Syntex, S. A., Laguna Mayran 413, Mexico City
SO Experientia (1953), 9, 62-3
CODEN: EXPEAM; ISSN: 0014-4754
DT Journal
LA English
OS CASREACT 48:3641
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 47, 12415g. Vigorous shaking of Δ4-cholesten-3β-ol or Δ4-22a-spirosten-3β-ol with freshly precipitated MnO2 resulted in conversion in satisfactory yield to the corresponding Δ4-3-ones in about 2 h. at room temperature Similar oxidation of Δ5-22a-spirostene- 3β,7α-diol 3-acetate produced the Δ5-7-one; Δ9(11)-22a-5α-spirostene-3β,12-diol gave the Δ9(11)-12-one; and Δ5,17(20)-pregnadiene-3β,21-diol gave the corresponding 21-aldehyde, all in satisfactory yield. Δ4-cholestene-3β,6β-diol in C6H6 with MnO2 at room temperature was oxidized only at C-3 producing Δ4-cholesten-3-one-6β-ol at 75% yield. This procedure has been used also to produce 6β-hydroxyprogesterone

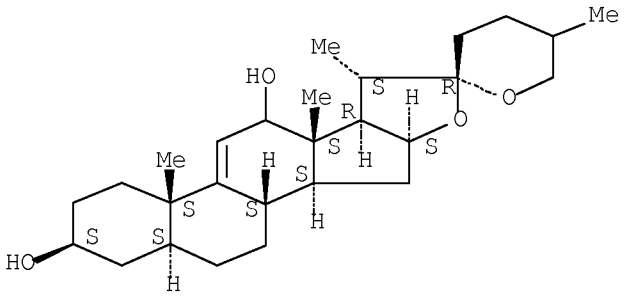
(m. 181-3°, [α]20D 105°, all rotations in CHCl3, λEtOHmax. 236 mμ, log ε 4.22) and 6β-hydroxy-Δ4-androstene-3,17-dione (m. 192-4°, [α]20D 114°, λEtOHmax. 236 mμ, log ε 4.25). At reflux temperature this reaction produced the corresponding diketones. Δ4-androstene-3,17-dione was reduced with LiAlH4 to a presumed mixture of Δ4-androstene-3β,17β-diol and the 3α,17β-diol which in CHCl3 with MnO2 at room temperature was only oxidized at C-3 to yield pure testosterone in 90% overall yield. The readily available Δ5-3β-ols (Type I) with MnO2 in refluxing C6H6 were found to yield the corresponding Δ4,6-dien-3-ones (Type III) in conversions of about 30%. In this way the following dienones (Type III) were prepd: Δ4,6-22a-spirostadien-3-one, Δ4,6-cholestadien-3-one, Δ4,6-androstadiene-3,17-dione, Δ4,6-androstadien-17β-ol-3-one (6-dehydrotestosterone), Δ4,6-pregnadiene-3,20-dione (6-dehydroprogesterone), Δ4,6-pregnadien-20β-ol-3-one (m. 197-9° [α]20D 15°, λEtOHmax. 282 mμ, log ε 4.54), Δ4,6,16-pregnatriene-3,20-dione (from Δ5,16-pregnadiene- 3β,20β-diol) (m. 253-6°, [α]20D 144°, λEtOHmax. 240 and 284 mμ, log ε 4.21 and 4.53), Δ4,6-pregnadien-17α-ol-3,20-dione (m. 240-2°, [α]20D 21°, λEtOHmax. 284 mμ, log ε 4.53), Δ4,6 pregnadien-21-ol-3,20-dione acetate, and Δ4,6-pregnadiene- 17α,21-diol-3,20-dione 21-acetate (6-dehydro Reichstein's Substance S acetate) (m. 218-20°, [α]20D 104°, λEtOHmax. 284 mμ, log ε 4.48). The reactions appear to pass through intermediates such as II.

IT 911461-28-4, 5α,22a-Spirost-9(11)-ene-3β,12-diol
(oxidation with manganese dioxide)

RN 911461-28-4 HCAPLUS

CN 5α,22a-Spirost-9(11)-ene-3β,12-diol (5CI) (CA INDEX NAME)

Absolute stereochemistry.

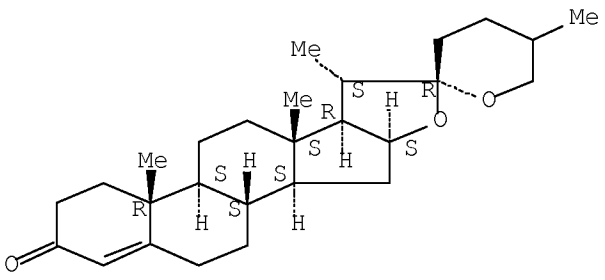


IT 7662-01-3P, 22a-Spirost-4-en-3-one 37147-71-0P, 22a-Spirosta-4,6-dien-3-one 882741-52-8P, 5α,22a-Spirost-9(11)-en-12-one, 3β-hydroxy-
RL: PREP (Preparation)
(preparation of)

RN 7662-01-3 HCAPLUS

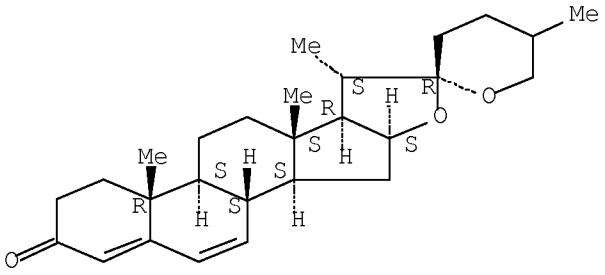
CN Spirost-4-en-3-one (9CI) (CA INDEX NAME)

Absolute stereochemistry.



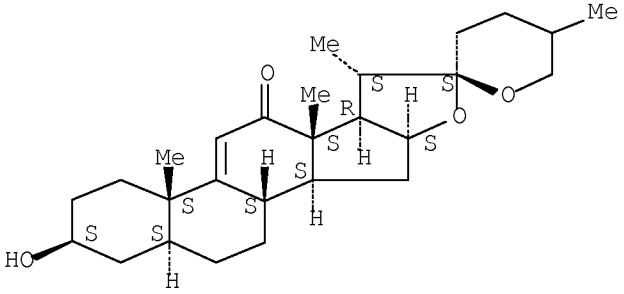
RN 37147-71-0 HCAPLUS
CN Spirosta-4,6-dien-3-one (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 882741-52-8 HCAPLUS
CN INDEX NAME NOT YET ASSIGNED

Relative stereochemistry.



L97 ANSWER 15 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1953:72869 HCAPLUS Full-text
DN 47:72869
OREF 47:12412c-i,12413a-e
TI The transformation of manogenin to hecogenin
AU Wendler, N. L.; Slates, H. L.; Tishler, M.
CS Merck & Co., Inc., Rahway, NJ
SO Journal of the American Chemical Society (1952), 74, 4894-7
CODEN: JACSAT; ISSN: 0002-7863
DT Journal

LA Unavailable
OS CASREACT 47:72869
GI For diagram(s), see printed CA Issue.
AB To 37.5 g. crude manogenin (I) containing 40-50% Δ9-dehydro derivative and varying amts. of gitogenin in 3 l. refluxing BuOH was added 75 g. Na portionwise as rapidly as possible, part of the BuOH removed in vacuo after 1-2 h. and the remainder as an azeotrope with H2O, H2O added to the residue, and the solid filtered and washed alkali-free to yield 35.6 g. agavogenin (II), feathery needles, m. 240-2° (from CHCl3EtOAc). II refluxed 1 h. with Ac2O gave the triacetate, m. 221-7° (from MeOH). II (35.5 g.) in 300 cc. dry pyridine heated 3 h. at 100°, under N, with 48 g. succinic anhydride, the mixture cooled, the pyridine removed in vacuo, the residue shaken with H2O and CHCl3, the aqueous layer extracted 3 times with CHCl3, and the combined CHCl3 extract washed with 2.5N HCl, H2O, and saturated aqueous NaCl, dried and evaporated in vacuo, yielded 53 g. II bis(hemisuccinate) (III), not further purified. Crude III (53 g.) in 500 cc. AcOH oxidized at room temperature with 5.87 g. CrO3 in 30 cc. 30% aqueous AcOH, the excess CrO3 destroyed with MeOH, the solution concentrated to a small volume in vacuo, diluted with H2O, extracted with CHCl3-Et2O, the extract washed with dilute H2SO4 and saturated aqueous NaCl, dried, and evaporated in vacuo, the residue (47 g.) dissolved in 1 l. MeOH containing 100 cc. H2O and 100 g. KOH, the solution refluxed 4 h., the MeOH removed in vacuo, H2O added, and the product extracted with CHCl3 yielded 20.5 g. I, m. 254-7° (from CHCl3EtOAc), containing some gitogenin. I (20 g.) in 200 cc. pyridine let stand 16 h. at 0-5° with 20 cc. MeSO2Cl and the mixture poured with stirring into ice water gave 21.7 g. I dimesylate (methanesulfonate) (IV), long slender needles, m. 241° (decomposition) (from Me2CO), [α]D24.5 -44.2° (CHCl3). IV (6.1 g.) heated 24 h. at 100° in a glass-lined autoclave with 15.25 g. NaI in 250 cc. dry Me2CO, the mixture filtered, the residue washed with Et2O and CHCl3, the combined filtrate and washings concentrated in vacuo, and the residue diluted with CHCl3 and Et2O, washed with 5% aqueous Na2S2O3 and H2O, dried, and evaporated gave 3.75 g. crystals, m. 173-5°; 2.00 g. of the crystalline product in petr. ether chromatographed on acid-washed Al2O3 gave 800 mg. Δ2-isoallospirosten-12-one (V), micalike plates, m. 199-200° (from aqueous Me2CO), [α]D24.5 39.1° (CHCl3). Similarly hecogenin mesylate, m. 178°, was prepared and converted with NaI in Me2CO, at 100° for 24 h., to V. From the mother liquor, of V, was obtained 950 mg. Δ2-22-isoallospirostene (VI), needles, m. 186-7° (from Me2CO), giving a yellow color with C(NO2)4. Hecogenone (VII) (500 mg.), 6.0 g. KOH, 60 cc. (CH2OH)2, and 0.6 cc. 85% N2H4.H2O heated cautiously to 140°, then 1 h. at 140°, and 1 h. at 190-5° while a slow stream of N was passed over the surface, poured into H2O, and the precipitate washed alkali-free yielded 350 mg. 22-isoallospirostane (VIII), plates, m. 173-4°, [α]D24.5 -61.8° (CHCl3); also obtained by hydrogenation of VI in EtOAc over PtO2. To 1 g. V in 15 cc. C6H6 was added, at 5°, 5 cc. C6H6 containing 0.3 g. BzO2H, the mixture diluted with 100 cc. Et2O, washed with cold 5% aqueous Na2CO3 and H2O, and the Et2O solution dried and evaporated to give 1.1 g. crude 2(α),3(α)-epoxy-22-isoallospirostan-12-one (IX), chromatographed on basic Al2O3 and recrystd. twice from Et2O, m. 210-13°, [α]D25 22° (CHCl3). To 400 mg. LiAlH4 in 100 cc. dry Et2O was added with vigorous stirring 1.1 g. IX in 20 cc. C6H6 and 40 cc. Et2O, the mixture stirred 45 min. at room temperature, then refluxed 10 min., the excess hydride decomposed with H2O and dilute HCl, the aqueous layer extracted with Et2O, and the combined Et2O layer and extract were washed acid-free with H2O and saturated aqueous NaCl, dried, and evaporated to give 1.05 g. crude compound (X) in 20 cc. AcOH oxidized overnight at room temperature with 358 mg. CrO3 in 15 cc. 80% AcOH gave 350 mg. VII, m. 238-41°, [α]D24.5 23.8° (CHCl3); an addnl. 200 mg. VII was obtained from the mother liquor. VII (1.7 g.) in 75 cc. dry THF reduced with 1.5 g. LiAlH4 gave crude compound (XI), which was dissolved in 20 cc. dry pyridine containing 3.0 g. succinic anhydride heated 3 h. on a steam bath under N, the mixture concentrated in

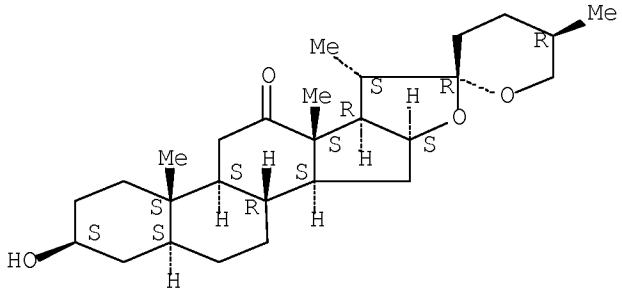
vacuo, diluted with H2O, extracted with CHCl3 and Et2O, and the extract washed with dilute HCl, H2O, and saturated aqueous NaCl, dried, and evaporated in vacuo to give 2.4 g. crude XI 3-hemisuccinate (XII). XII (2.4 g.) in 50 cc. AcOH oxidized 16 h. at room temperature with 350 mg. CrO3 in 10 cc. 80% aqueous AcOH gave 2.16 g. crude hecogenin (XIII) hemisuccinate, which refluxed 4 h. under N with 75 cc. MeOH containing 4.0 g. KOH yielded 650 mg. XIII, small plates, m. 263-6°, [α]D24.5 13.5° (CHCl3); acetate, m. 247-50° (from CHCl3-EtOAc), [α]D24.5 92° (CHCl3).

IT 467-55-0, Hecogenin
(and esters)

RN 467-55-0 HCAPLUS

CN Spirostan-12-one, 3-hydroxy-, (3β,5α,25R)- (CA INDEX NAME)

Absolute stereochemistry.

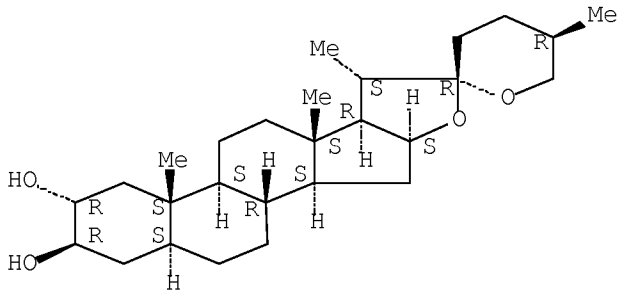


IT 511-96-6P, Gitogenin 564-43-2P, Manogenin 2137-20-4P, Hecogenone 883721-07-1P, 22-Isoallospirostan-3α,12-diol
RL: PREP (Preparation)
(preparation of)

RN 511-96-6 HCAPLUS

CN Spirostan-2,3-diol, (2α,3β,5α,25R)- (CA INDEX NAME)

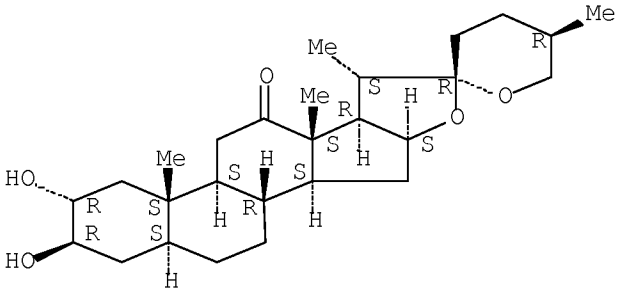
Absolute stereochemistry.



RN 564-43-2 HCAPLUS

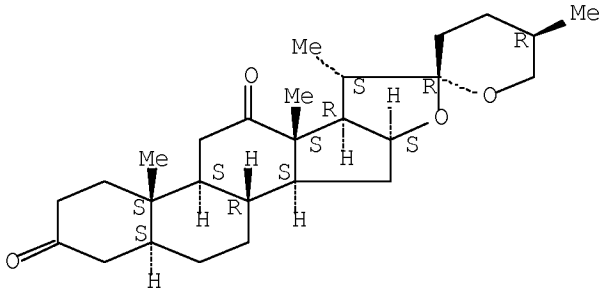
CN Spirostan-12-one, 2,3-dihydroxy-, (2α,3β,5α,25R)- (CA INDEX NAME)

Absolute stereochemistry.



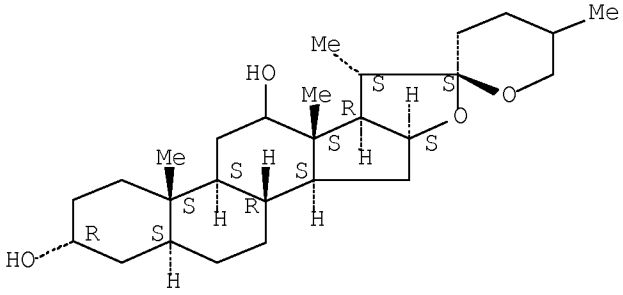
RN 2137-20-4 HCAPLUS
CN Spirostan-3,12-dione, (5α,25R)- (CA INDEX NAME)

Absolute stereochemistry.



RN 883721-07-1 HCAPLUS
CN 22-Isoallospirostan-3α,12-diol (5CI) (CA INDEX NAME)

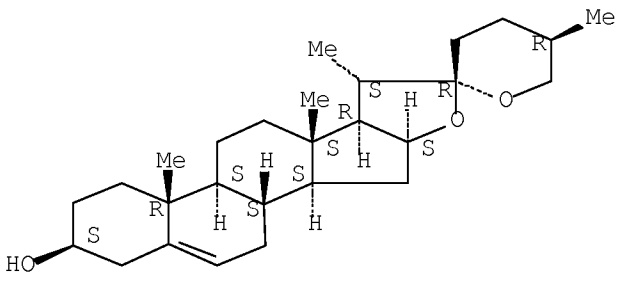
Absolute stereochemistry.



L97 ANSWER 16 OF 16 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1941:18004 HCAPLUS Full-text
DN 35:18004
OREF 35:2899c-i,2900a-b
TI Sterols. CXV. Sapogenins. 44. Relation diosgenin and cholesterol
AU Marker, Russell E.; Turner, D. L.
SO Journal of the American Chemical Society (1941), 63, 767-71
CODEN: JACSAT; ISSN: 0002-7863

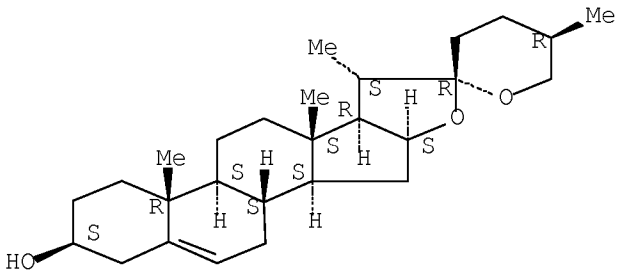
DT Journal
LA Unavailable
AB The assumption that the C skeleton of the side chain in the steroidal sapogenins is identical with that of cholesterol (I) has been based on the isolation of α-methylglutaric acid from the oxidation products of digitogenic acid and the occurrence of Me isohexyl ketone (?) in the reaction products of Se with sarsasapogenin; this assumption has now been proved by converting diosgenin (II) into I and addnl. evidence is afforded for the 5,6-position of the double bond in II. Reduction of 5 g. II with 150 g. amalgamated Zn in 500 cc. EtOH and 150 cc. concentrated HCl for 3 hrs. gives 3 g. of tetrahydrodiosgenin (III), m. 178-9°; triacetate (IV), m. 119.5°; IV is saponified by EtOH-KOH to III; tribenzoate of III, m. 166-7°. Catalytic reduction with PtO_2 of III, using 3 atmospheric of H for 2 hrs., gives tetrahydrotigogenin (3,16,27-trihydroxycholestane) (V), m. 195-7°; catalytic reduction of IV or acetylation of V gives the tri-Ac derivative of V, m. 67-8°, tribenzoate of V, m. 162°. Refluxing 4 g. of IV in 25 cc. C_6H_6 with 2 g. H_2SeO_3 in 75 cc. 97% AcOH for 1 hr., adding 5 g. AcOK and refluxing for 10 min. give after hydrolysis with EtOH-KOH 0.5 g. of a tetrahydroxycholestene, $C_{27}H_{46}O_4$, m. 196°, which is converted by refluxing 1 g. with 5 cc. concentrated HCl in 100 cc. EtOH into Δ4-3-keto-16,27-dihydroxycholestene, $C_{27}H_{44}O_3$, m. 163-4°. Refluxing 4 g. III and 12 cc. PBr_3 in 300 cc. C_6H_6 for 2 hrs., purification of the product by washing the ether solution with H_2O and Na_2CO_3 and refluxing the residue (4.7 g.) in 150 cc. AcOH with 600 mg. AcOK with final reduction with Na in PrOH give Δ5-cholestene, m. 89-91°, and I, separated by sublimation (80-100° and 120-40°). Oxidation of 25 g. diosgenin acetate (VI) with CrO_3 in AcOH at 50-3° gives 4.4 g. unchanged VI, 50 mg. of an acid, $C_{27}H_{40}O_5$, decompose 226°, and 7-ketodiosgenin acetate (VII), m. 197° [semicarbazone (VIII), decompose 282°]. The Wolff-Kishner reaction with VIII gives a small quantity of 3,5-dehydrodesoxytigogenin. VII with 15% EtOHKOH (15 min. on the steam bath) gives 3,5-dihydro-7-ketotigogenin, m. 197-8°. Addition of 170 cc. HCl during 2.5 hrs. to 3 g. 4-dehydrotigogenone (IX) and 100 g. Zn-Hg in 500 cc. EtOH at the b. p. gives 500 mg. of 4-dehydrodesoxytigogenin, m. 145.5-6°; it also is formed with unamalgamated Zn. IX (5 g.) on reduction with $(iso\text{-}PrO)_3Al$ in iso-PrOH gives 2.5 g. of 3,5-dehydrodesoxytigogenin, m. 168-9°; catalytic reduction yields desoxytigogenin, m. 173°. II (3 g.) and 17 g. $p\text{-}C_6H_4O_2$ in 200 cc. PhMe, from which 50 cc. of the PhMe is removed in vacuo, treated with 5 g. $(iso\text{-}PrO)_3Al$ and refluxed 1 hr. give 0.9 g. of 4,6-dehydrotigogenone, m. 205-7°, which is purified by filtration through Al_2O_3 and treatment with succinic anhydride and C_6H_5N to remove carbinols. II gives chlorodesoxydiosgenin, m. 211-13°; catalytic reduction in AcOH yields 3-chlorodesoxytigogenin (X), m. 204-7°; reaction of 5 g. tigogenin in 100 cc. $CHCl_3$ containing 5 g. $CaCO_3$ with 5 g. PCl_5 gives 2.8 g. of an isomer(?) (XI) of X, m. 210-12° (mixed m. p. with X, 189-204°). Refluxing 1.3 g. XI with 30 cc. quinoline for 1 hr. gives 350 mg. of 2-dehydrodesoxytigogenin, m. 163-6°. Refluxing 5 g. 4-dehydrotigogenone and 15 g. $(iso\text{-}PrO)_3Al$ in 500 iso-PrOH for 6 hrs., distilling slowly for 24 hrs. and rapidly to 0.5 its volume, cooling, adding 300 cc. cold 8% MeOH-KOH and after 1 hr. pouring into H_2O, gives 1.1 g. of 4-dehydroepitigogenin, m. 208-10°; this is not precipitated by digitonin; refluxing with Ac_2O for 30 min. gives Δ3,5-desoxytigogenin; the material from the digitonin precipitate gives a compound, m. 167-9°, which is dehydrated by heating in vacuo at 100° and then m. 125-37°.
IT 512-04-9, Diosgenin
(and derivs.)
RN 512-04-9 HCAPLUS
CN Spirost-5-en-3-ol, (3β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



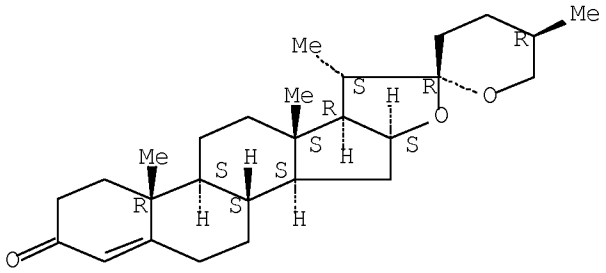
IT 512-04-9P, Diosgenin 6870-79-7P, Tigogenone, 4-dehydro-
16653-68-2P, Tigogenone, 4,6-dehydro-
RL: PREP (Preparation)
(preparation of)
RN 512-04-9 HCAPLUS
CN Spirost-5-en-3-ol, (3β,25R)- (CA INDEX NAME)

Absolute stereochemistry.



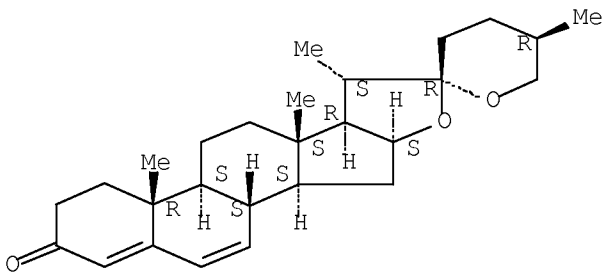
RN 6870-79-7 HCAPLUS
CN Spirost-4-en-3-one, (25R)- (CA INDEX NAME)

Absolute stereochemistry.



RN 16653-68-2 HCAPLUS
CN Spirosta-4,6-dien-3-one, (25R)- (CA INDEX NAME)

Absolute stereochemistry.



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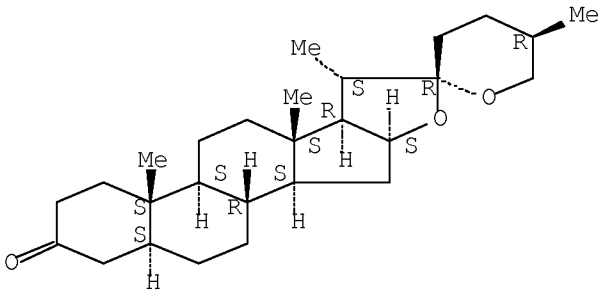
L105 ANSWER 1 OF 1 HCAPLUS COPYRIGHT 2007 ACS on STN
AN 1942:37236 HCAPLUS Full-text
DN 36:37236
OREF 36:5828f-h
ED Entered STN: 16 Dec 2001
TI Sterols. CXLVII. Sapogenins. 61. The bioreduction of steroids
AU Marker, Russell E.; Wagner, R. B.; Ulshafer, Paul R.
SO Journal of the American Chemical Society (1942), 64, 1653-5
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
CC 10 (Organic Chemistry)
AB cf. C. A. 36, 4516.3. From the feces of a 10-kg. dog, fed a mixture of 150 g. of meat, 50 g. of pig brain and 3 g. of diosgenin (I) for 3 consecutive days, there were isolated 5.2 g. of I, 0.2 g. of epismilagenin (II) and 0.1 g. of smilagenin (III) (as acetate). Similarly, tigogenone gives tigogenin and epitigogenin and sarsa apogenone yield sarsasapogenin and episarsasapogenin. This and earlier results (C. A. 36, 3182.9) support the hypothesis of Schoenheimer (C. A. 29, 353.4) that there is a reversible biol. reaction of the type cholestenone cholesterol. δ4-Dehydrotigogenone may be reduced by 1 enzyme system to II and III and by another system to I. The fact that HO compds. of both α- and β-configuration are formed is contrary to earlier statements (C. A. 32, 7471.9) that reduction in vivo of 3-ketosteroids appears to give only a compds.
IT Sapogenins
Sapogenins
Sterols
IT Steroids
(bioreduction of)
IT Animal organism
(steroid reduction in)
IT 470-07-5, Tigogenone 512-04-9, Diosgenin
639-96-3, Sarsasapogenone
(fate in animal organism)
IT 126-18-1P, Smilagenin 16653-88-6P, Epismilagenin
RL: PREP (Preparation)
(formation in animal organism from diosgenin)
IT 126-19-2P, Sarsasapogenin 470-03-1P, Episarsasapogenin
RL: PREP (Preparation)
(formation in animal organism from sarsasapogenone)
IT 77-60-1P, Tigogenin 6788-40-5P, Epitigogenin
RL: PREP (Preparation)
(formation in animal organism from tigogenone)

IT 470-07-5, Tigogenone 512-04-9, Diosgenin
639-96-3, Sarsasapogenone
(fate in animal organism)

RN 470-07-5 HCAPLUS

CN Spirostan-3-one, (5α,25R)- (CA INDEX NAME)

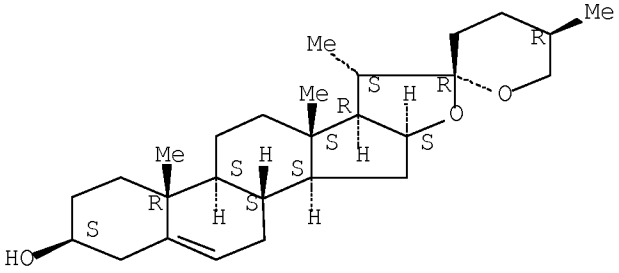
Absolute stereochemistry.



RN 512-04-9 HCAPLUS

CN Spirost-5-en-3-ol, (3β,25R)- (CA INDEX NAME)

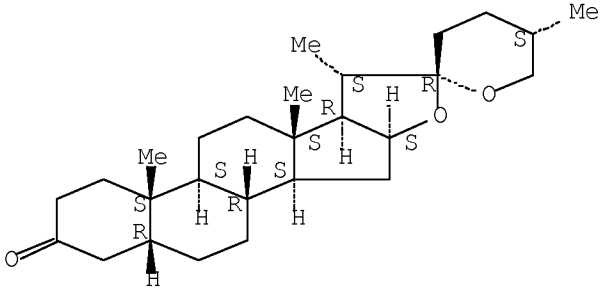
Absolute stereochemistry.



RN 639-96-3 HCAPLUS

CN Spirostan-3-one, (5β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



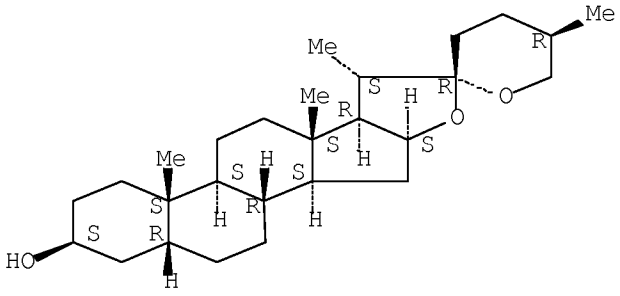
IT 126-18-1P, Smilagenin 16653-88-6P, Epismilagenin
RL: PREP (Preparation)

(formation in animal organism from diosgenin)

RN 126-18-1 HCAPLUS

CN Spirostan-3-ol, (3β,5β,25R)- (CA INDEX NAME)

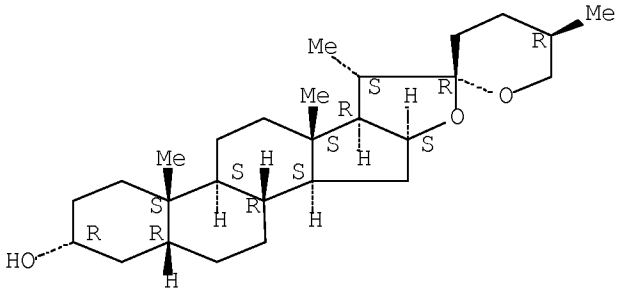
Absolute stereochemistry.



RN 16653-88-6 HCAPLUS

CN Spirostan-3-ol, (3α,5β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



IT 126-19-2P, Sarsasapogenin 470-03-1P, Episarsasapogenin

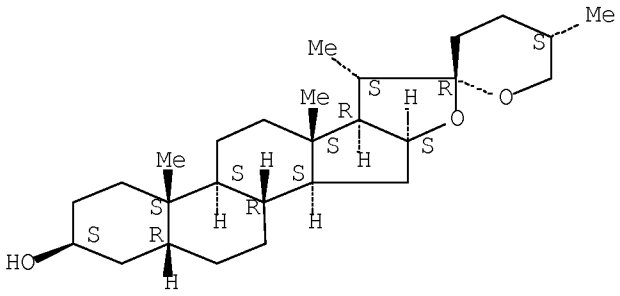
RL: PREP (Preparation)

(formation in animal organism from sarsasapogenone)

RN 126-19-2 HCAPLUS

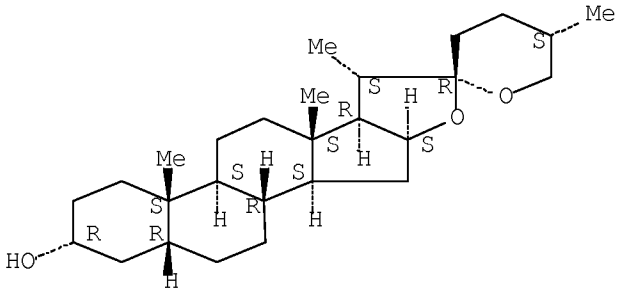
CN Spirostan-3-ol, (3β,5β,25S)- (CA INDEX NAME)

Absolute stereochemistry.



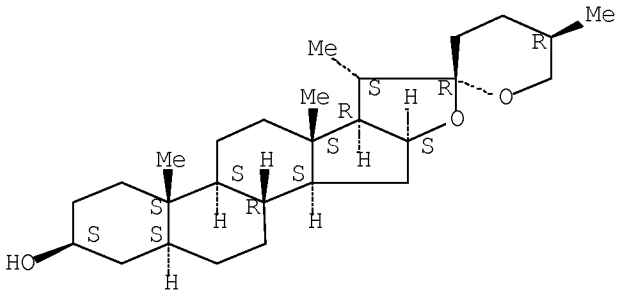
RN 470-03-1 HCAPLUS
CN Spirostan-3-ol, (3α,5β,25S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



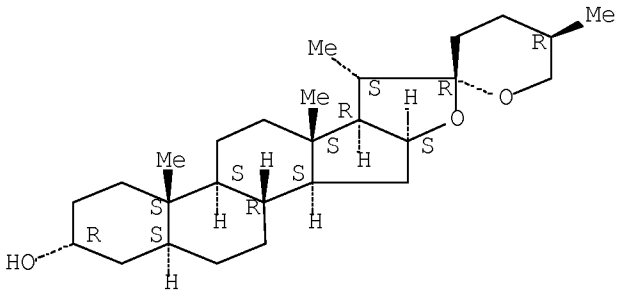
IT 77-60-1P, Tigogenin 6788-40-5P, Epitigogenin
RL: PREP (Preparation)
(formation in animal organism from tigogenone)
RN 77-60-1 HCAPLUS
CN Spirostan-3-ol, (3β,5α,25R)- (CA INDEX NAME)

Absolute stereochemistry.



RN 6788-40-5 HCAPLUS
CN Spirostan-3-ol, (3α,5α,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



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L3             STR L1
L4            10 S L3 CSS SAM SUB=L2
L5           134 S L3 CSS FUL SUB=L2
               SAV L5 NOBLE531D/A
L6            17 S L5 AND 5 BETA
L7           117 S L5 NOT L6
L8           131 S L5 NOT (T/ELS OR 14C#)
L9             STR L3
L10           13 S L9 CSS SAM SUB=L2
L11          351 S L9 CSS FUL SUB=L2
               SAV L11 NOBLE351E/A
L12           23 S L11 AND NC>=2
L13          328 S L11 NOT L12
L14          295 S L13 NOT ((D OR T)/ELS OR 11C# OR 13C# OR 14C# OR C11# OR C13#
L15           12 S L14 AND IDS/CI
L16          283 S L14 NOT L15
L17            3 S L16 AND NR>=7
L18          280 S L16 NOT L17
L19            STR L9
L20           14 S L19 CSS SAM SUB=L2
L21            STR L19
L22           16 S L21 CSS SAM SUB=L2
L23          324 S L21 CSS FUL SUB=L2
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L26           52 S L25 NOT L24
L27          299 S L23 NOT ((D OR T)/ELS OR 11C# OR 13C# OR 14C# OR C11# OR C13#
L28          235 S L27 NOT L24-L26
L29            STR L9
L30         2505 S L29 CSS FUL SUB=L2
L31            STR L9
L32          352 S L31 CSS FUL SUB=L30
L33            1 S L32 NOT L11
L34            STR L21
L35          339 S L34 CSS FUL SUB=L2
L36           15 S L35 NOT L32,L23
L37           14 S L36 NOT 14C
L38            4 S 126-18-1 OR 470-03-1 OR 16653-88-6 OR 126-19-2
L39            1 S 512-04-9
L40            1 S 6870-79-7

     FILE 'HCAPLUS' ENTERED AT 07:24:48 ON 13 DEC 2007
L41         2288 S L39 OR DIOSGENIN
L42           91 S L40 OR DIOSGENONE
L43           57 S L41 AND L42
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L44          18 S L43 AND (REDUC? OR REDOX)
                E REDOX/CT
                E E34+ALL
L45       27061 S E9,E10,E11,E17
                E E9
                E E11+ALL
L46      139018 S E2-E4,E34,E35,E42,E43
                E E34+ALL
L47      113307 S E3-E5
L48           2 S L43 AND L45-L47
L49          16 S L44 NOT L48
L50          16 S L44 AND PY<=2002 NOT P/DT
L51           2 S L44 AND (PD<=20021028 OR PRD<=20021028 OR AD<=20021028) AND P
L52           2 S L48 AND L50,L51
L53          16 S L50,L51 NOT L52
                SEL AN 2 12
L54           2 S E1-E4 AND L53
L55           4 S L48,L54
L56           4 S L55 AND L41-L55
L57           2 S L56 AND (?SARSASAPOGENIN? OR ?EPISARSASAPOGENIN? OR ?SMILAGEN
L58           2 S L56 AND L38
L59           2 S L57,L58
L60           4 S L56,L59
                SEL RN

     FILE 'REGISTRY' ENTERED AT 07:37:19 ON 13 DEC 2007
L61          30 S E5-E34
L62           8 S L61 AND (B OR AL)/ELS
L63           4 S L61 AND L8
L64           5 S L61 AND L18,L38
L65           6 S L61 AND L38,L39,L40
L66           2 S L61 AND L26,L28,L37
L67          11 S L61 NOT L62-L66

     FILE 'HCAPLUS' ENTERED AT 07:38:18 ON 13 DEC 2007
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L69           1 S L68 AND LIALH4
L70           1 S L68 AND AL2O3
L71           4 S L68-L70

     FILE 'REGISTRY' ENTERED AT 07:39:32 ON 13 DEC 2007

     FILE 'HCAPLUS' ENTERED AT 07:40:03 ON 13 DEC 2007
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L73         193 S L72 AND (L18 OR L38 OR L28 OR L26 OR L37)
L74         164 S L73 AND PY<=2002 NOT P/DT
L75          15 S L73 AND (PD<=20021028 OR PRD<=20021028 OR AD<=20021028) AND P
L76         179 S L74,L75
L77           3 S L76 AND L45-L47
L78           0 S L76 AND REDOX
L79          48 S L76 AND REDUC?
L80          48 S L77,L79
L81           1 S L80 AND L62
L82          22 S L80 AND (LIALH4 OR AL2O3 OR ?BORON? OR ?BORAN? OR ?BORIC? OR
L83          22 S L81,L82
L84          46 S L80 NOT L71

     FILE 'REGISTRY' ENTERED AT 07:42:33 ON 13 DEC 2007

     FILE 'HCAPLUS' ENTERED AT 07:42:33 ON 13 DEC 2007
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L85             TRA L84 1- RN :     1015 TERMS

     FILE 'REGISTRY' ENTERED AT 07:42:35 ON 13 DEC 2007
L86         1015 SEA L85
L87            1 S L86 AND (B OR AL)/ELS
L88            1 S L86 AND (BORON? OR BORAT? OR BORIC? OR ?ALUMIN?/CNS)
L89            1 S L87,L88

     FILE 'HCAPLUS' ENTERED AT 07:43:22 ON 13 DEC 2007
L90            1 S L89 AND L80
L91           22 S L83,L90
L92           18 S L91 AND (L18 OR L38 OR L28 OR L26 OR L37)(L)PREP+NT/RL
L93            3 S L91 AND L8 (L) RACT+NT/RL
L94            2 S L92 AND L93
L95            1 S L94 NOT L71
L96           17 S L92,L93 NOT L94,L71
L97           16 S L96 AND L18,L38
L98           20 S L83 NOT L71,L95
L99            1 S L98 AND L8(L)RACT+NT/RL
L100          16 S L98 AND (L18 OR L38 OR L28 OR L26 OR L37)(L)PREP+NT/RL
L101           0 S L99 AND L100
L102          25 S L80 NOT L71,L95,L100,L98
                 SEL AN 21
L103           1 S L102 AND E35-E36
L104           2 S L99,L103
L105           1 S L104 NOT L71,L95,L97

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